THE GLASS INDUSTRY

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G. C. M. I. HOLDS ANNUAL MEETING IN ASHEVILLE, NORTH CAROLINA

The annual meeting of the Glass Container Manufacturers Institute convened at Grove Park Inn in Asheville, North Carolina, for a three day session and was called to order by President George F. Lang at 7 P.M. Wednesday, April 30.

At this point it should be mentioned that at this meeting a new president was elected, Mr. Robert L. Warren of Brockway Glass Company. Mr. Lang had served for two years, a tenure of office which he emphatically stated, in his opinion, should not be exceeded by any president. During his term of office, Mr. Lang served his industry with the highest degree of energy, foresight and human undertanding of the problems confronting his fellow glass manufacturers. That his zeal in guiding the affairs of the Institute was appreciated by the entire membership was outstandingly evident by the eulogies which he received at the formal announcement of his retirement. The institute will continue to benefit from George Lang's services since he remains a member of the Board of Trustees at least until 1949. Mr. Lewis F. Gayner and Mr. J. R. Macdonald were reelected to the Board of Trustees for a term of three years.

George F. Lang

Robert L. Warren

Following the opening remarks of the President, the usual pattern of the Institute's meetings was followed by the presentation of the reports of the nine standing committees by either Committee Chairmen or an alternate.

The first of these reports was from the Committee on Labor Relations and since Mr. L. C. Roche, Chairman of the Committee, was unable to attend the meeting, labor matters were broadly presented by Mr. Ralph A. Lind, Secretary of the Labor Committee.

Mr. B. H. Taylor, Traffic Director of the G.C.M.I., was next on the program to present the report of the Traffic Committee whose Chairman is Mr. I. L. Dunnington of the Anchor Hocking Glass Corporation. He touched broadly on the activities of the Traffic Committee but emphasized the work of the Committee on the vexing problem of the efforts of the railroads to revise Consolidated Freight Classification Rule No. 41. This rule pertains to fibreboard shipping containers and inner packing for glass containers and glass-packed products.

In connection with this specific traffic matter, high praise is due Mr. Taylor and the Traffic Committee in bringing about an agreement between the carriers on the one hand and the packers and glass container manufacturers on the other; an agreement much more favorable to the glass container industry than would have been the case had the railroad's original proposals obtained.

Space limitations do not permit a detailed account of the tremendous amount of work involved in this particular traffic matter, but an outline of the agreement

as stipulated at a hearing held before the Interstate Commerce Commission April 22 in New York may be stated as follows.

The revised Rule 41 will go into effect June 15, 1947. It contains a provision that boxes manufactured before the effective date will be accepted by the railroads for a period of six months, after which all boxes must comply. Full details affecting glass-packed products appear in the June issue of THE GLASS PACKER, The Glass Industry's sister publication.

The version of Rule 41 now in effect and to be replaced in June contains no specifications for inner packing providing only that these must be "adequate." The rule had been relaxed twice since 1941, based on good shipping experience with glass containers. The railroads, however, were alarmed by a steadily mounting volume of loss and damage claims since the start of the war and attributed a large portion of them to inferior fibre shipping containers and insufficient inner packing. These carriers began trying in 1943 to have the rule changed to require much heavier boxes and certain inner packing for glassware and glass-packed products.

When the Eastern railroads attempted to revive the rule by tariff publication in November, 1946, the publication was suspended by the ICC on petitions filed by 1,485 protestants. Of these protestants, the glass container industry was by far the most important because it supplies about 85 per cent of the complete fibre boxes, including inner packing, used by glass packers, through the long established trade practice of shipping empty glass containers in cartons which are used as re-shipping containers for glass-packed products. After securing this suspension in the case of the Eastern railroads, the G.C.M.I. persuaded the Western and Southern railroads to continue the existing Rule 41 voluntarily for the first six months of 1947, so that studies could be completed on which sound recommendations could be based. These recommendations were submitted at the April meeting and the revised Rule 41 emerged as a result.

Further indication of the extensive work carried on by the Glass Container Manufacturers Institute in connection with Rule 41 was evidenced by a brief talk by Dr. Frank W. Preston in which he described some of the work done by Preston Laboratories in collaboration with the Traffic Committee on the subject.

Dr. Preston pointed out some things which should be corrected by glass manufacturers and packers and also pointed out some of the shortcomings of the railroads in matters of handling. In summing up his findings, he urged cooperation with shippers and the railroads, education of shippers and collaboration of all the parties concerned.

Mr. Arthur S. Reece, Chairman of the Committee on Package Design and Specifications, followed Dr. Preston with the report of his Committee. For the most part, Mr. Reece's report dealt with his Committee's work in connection with the requirements for fibre shipping containers under the originally proposed Rule No. 41.

Mr. Reece described the work of the Package Design and Specifications Committee with that of the Traffic Committee and also outlined the activity by his Committee in developing interior packing specifications as would be acceptable to the industry. Also touched upon in Mr. Reece's report was the study conducted by the Owens-Illinois Glass Company in collaboration with other glass manufacturers with regard to the effect of concentration of load on corrugated fibreboard in order to evaluate protection afforded by different types of inner packing material and the effect their method of application would have upon the crushing and impact forces that might be expected.

In closing his report, Mr. Reece emphasized his Committee's attitude with regard to a sustained industry carton research program and reiterated the Committee's objectives in this matter. These objectives are: 1) The development of more basic information on materials entering into construction of fibre boxes; 2) a. The development of improved methods for evaluating serviceability of fibre boxes, b. The development of the most adaptable inner packing materials and manner of use to insure maximum protection to contents of fibre boxes; 3) The development of data for use in formulating recommendations to rail and motor carriers on tariff rules which fix requirements for packaging glass containers and articles in glass containers; 4) The development of information for use in considering the adoption of standards for fibre boxes and inner packing methods; 5) The development of data needed for the preparation of an industry fibre box manual; and 6) The development of facts suitable for use in advising with glass packers on specific packaging problems.

The activities of the Technical Committee on Glass Packed Products for the period from December, 1946, to May, 1947, were described by Committee Chairman, Dr. John M. Sharf of Armstrong Cork Company. The only change in the Committee's roster is the replacement of Mr. Ned Kentner by Mr. Albert Kok, both of White Cap Company.

Dr. Sharf chronicled various meetings which have been held for the primary purpose of considering mechanical details and arrangements of retorts and instrumentation. He also stated several conferences are contemplated with retort manufacturers representatives and the representatives of instrument manufacturers for the purpose of arriving at standardized retort arrangements as the basis for thermal processing studies and recommendations.

The research program at Massachusetts State College, Dr. Sharf stated, has continued along its customary high plane although the group has been somewhat shorthanded due to their active participation in the cooperative work with the National Canners Association in its West Coast Laboratories in San Francisco.

In concluding his report on past and future work of his Committee, Dr. Sharf stated, "The major services to be expected from this Committee will be ultimately the standardization of the processing times for non-acid foods packed in glass, a continuation of the excellent investigational work being carried on at Massachusetts State College, the continuation of the Food Technology Abstracts, and a continued interest in any new subjects which would warrant investigation relating to glass packed products."

The first day of the three day meeting was brought to a close with the report of Mr. Edward A. Schrag, Vice President of Knox Glass Associates and Chairman of the Committee on Market Research and Promotion.

While this Committee has been in existence since the

(*Continued on page* 320)

THE GLASS DIVISION AT ATLANTIC CITY

After an interval of nearly two decades, the American Ceramic Society returned to Atlantic City for its forty-ninth annual meeting, which was attended by a record registration of more than 1,650 members. About one-fifth of this number attended sessions of the Glass Division.

Gray skies, chill breezes and dashes of rain did nothing to make the occasion a pleasant outing. The technical sessions were held in the Convention Hall about a half-mile from the Traymore, headquarters hotel. This necessitated a bored walk of ten minutes, followed by a hunt and climb to the far upper corner of the huge building where the glass men found spacious segregation. The room was so large that the public address system became important and it was difficult for all to hear discussions from the floor. It was so distant that the "pages" assigned to operate the lantern did not always find the place and volunteers were substituted.

Otherwise, the sessions were excellently handled by Chairman O. G. Burch, Owens-Illinois Glass Company. He turned over the gavel at times to the Chairman-elect, R. F. Brenner, Anchor Hocking Glass Corporation, who had performed very well his task of arranging the program, and to Vice-Chairman-elect, H. R. Lillie, Corning Glass Works, who will head the program committee for next year.

The increasing size of the group attending the technical sessions of the Glass Division is gratifying to all who are interested in the industry because it demonstrates growing participation by executives, production men, technologists and students. However, size presents its own problems in arranging and conducting the sessions. These problems become more acute when the sessions are synchronized with those of other Divisions which compete for attention and are accompanied by the manifold attractions and interests of the Society's general meeting. Consequently, the Glass Division contemplates added emphasis on its Fall Meeting as an opportunity for the presentation and discussion of papers without distraction or interference.

Dr. H. R. Lillie

The consideration of size comes up again in connection with the mass of data that accumulates on the properties and behavior of glass. Answers to the question "how?" pile up so fast that the question "why?" seems to become more, rather than less, difficult to answer. This is particularly true of the problem of strength—breaking, if one prefers—of glass.

N. W. Taylor, Minnesota Mining and Manufacturing Corporation, made a commendable effort to correlate mathematically breaking stress and time of its application. Dr. Taylor held the attention of the members for more than an hour and a lively discussion followed his paper which could properly be called a lecture. Whether or not his treatment of the subject is finally accepted as tenable, he is to be commended for his bold foray into the theoretical field.

Several papers came from the laboratory of Glass Science, Inc., at Penn State, brought by students of Prof. W. A. Weyl. The presentation by Miss Evelyn C. Marboe was a good example of what can be done toward following the rules of the Society and the proposals of the Glass Division at its 1946 Fall Meeting. Brevity, clarity, avoidance of reading from manuscript and legibility of lantern slides received due attention. Miss Marboe explained the origin and nature of iron stains in bottles and showed how they could be prevented by using a solution which suppresses ferric ions by taking them into complex anions.

R. R. Shively, Jr., showed how minor ingredients help to produce selenium ruby glasses. The explanations were clear, but some statements needed support by experimental evidence. This was true particularly concerning zinc oxide, which is not generally believed to promote low-temperature mobility.

G. E. Rindone reported an interesting method of establishing oxidizing and reducing conditions in molten glasses by electrolysis. Presented only as a laboratory tool, this method might conceivably have industrial applications.

The National Bureau of Standards brought five papers. The first of these, given by J. M. Florence, contributed to our knowledge of heat transmission by some glasses of unusual composition. A. Q. Tool, renowned as he is for making complex matters appear simple by the off-hand manner in which he presents them, carried further the line of study of heat-treatment vs. density begun by him more than twenty years ago. Clearer notions about the frame-work of glass more lately developed enabled him to give more satisfactory explanations of the density changes.

The remaining Bureau papers dealt with surface tension. L. Shartsis, A. W. Smock and S. Spinner dealt with some low values for the lead borates. The treatment and analysis of the volatility problem was especially good. It would be highly desirable to deal as effectively with the problem of the lack of lead compounds in the raw materials market. Shartsis and Spinner showed values of surface tension about three times as high for lead silicates, ranging up to 236 dynes/cm. against 80 for the lead borates.

H. E. Simpson, New York State College of Ceramics,

James L. Crawford, C. L. Babcock and Paul M. Offill

J. F. Corkill and J. A. Hyland

presented a variation from the usual approach to the durability problem. He exposed different glasses to controlled, warm atmosphere at saturation, getting comparisons which might reasonably be held to compare with behaviors under evil service conditions.

Fine structure received application to the interpretation of kinks in the curves expressing property-temperature relationships in a paper by W. R. Ham, A. G. Pincus and C. N. Samans, American Optical Company. The tools of theory improve and their use may yet lead us out of some of the puzzles which have been so difficult to solve in the past.

Tools of a more tangible kind were discussed in two papers. V. L. Parsegian, Portable Products Corporation, gave a lecture on pyrometry. It was full of good reminders as to theory and practice, but the speaker evidently did not appreciate that most of his hearers were fairly conversant with those matters. Victor Paschkis, Columbia University, took the Division into the difficult field of heat flow. Analogy with the electric current in terms of potential, resistivity and capacity became useful in the explanation of heat-flow in devices used in the glass industry and in bodies made up of materials of different conductivities.

Donald Hubbard and G. F. Ryndes, Bureau of Standards, reported on some delicate measurements by interferometer methods of the swelling of glass in various solutions as the result of attack and its bearing on errors in work with glass electrodes.

Data on strontium-bearing glasses was presented by C. L. Babcock, Owens-Illinois Glass Company. Plant men might have felt inclined to ask where to get enough strontis to make a tank full of such glass. J. C. Coleman, also Owens-Illinois Glass Company, probably not the discoverer of the mineral, showed the effect of boron oxide on the major properties of glasses of container composition. His work could be regarded as a severely practical contribution.

Some surprising results appeared in the study by R. D. Smith and P. E. Corbin, Corning Glass Works, of the attack of alkaline solutions on glass. The fact that alkaline silicates are more corrosive than the hydroxides runs counter to preconceived notions. Maybe it should be explained on the homely basis that "them as has, gets."

P. W. Collyer, American Optical Company, used a period of 500 hours for some of his heat-treating studies, coming up with a reliable equation for finding how fast the index of refraction comes up toward its maximum value.

The practical utility of a piece of glassware is measured by the length of its service life. Some doctor has remarked that a man's lifetime is determined less by the number of years that have passed over his head than by the number of colds that have passed through it. In a similar view, if more seriously, J. T. Glathart and F. W. Preston show that the ability of a glass tumbler to take bumps before being bumped off depends upon how much scratching and abuse—a function of service age—have already made the thing vulnerable.

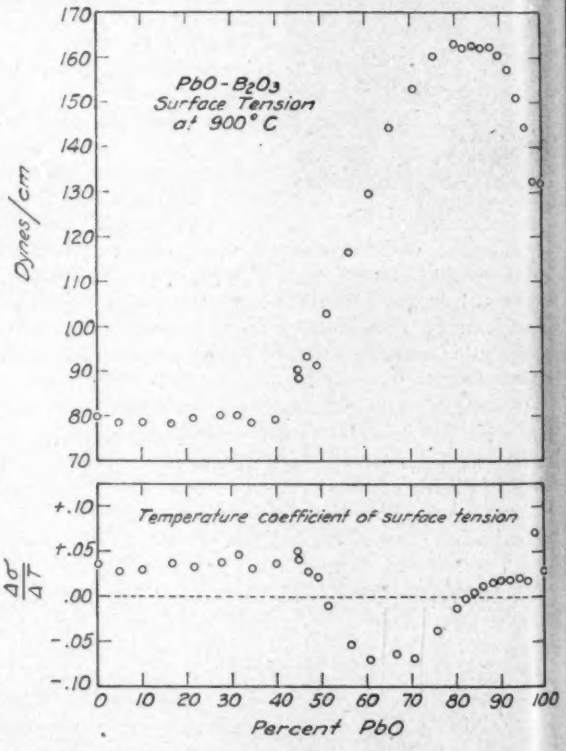
In the business session, the principal matters handled were the "research fund" and the proposed Third International Congress on Glass. Action taken at an earlier meeting was reconsidered and $300 was voted from the research fund to be given to the Society to help publish anew the phase-equilibrium diagrams. Dr. J. C. Hostetter, representative of the Division on the International Commission, was appointed to form a committee to consider and plan for the Congress to be held probably in 1949.

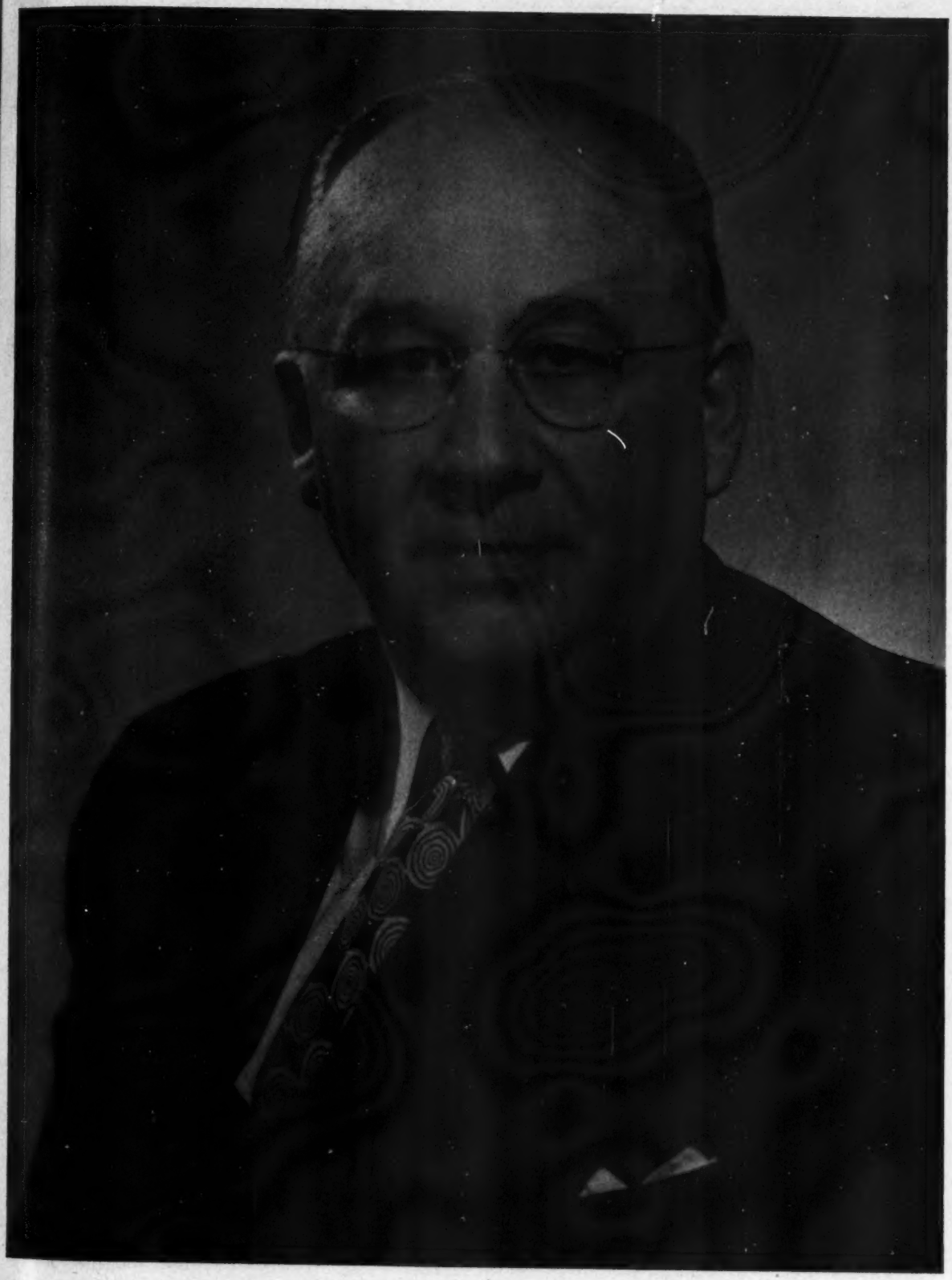
Fellows who were inducted at the annual meeting were Ralph F. Brenner, Anchor-Hocking Glass Corp.; Vincent Broomhall, Continental Kilns, Inc.; Ralph L. Cook, Professor of Ceramic Engineering, University of Illinois; Charles A. Freeman, A. P. Green Firebrick Company; Charles M. Harder, Professor, Department of Ceramic Engineering, Alfred University; Andrew L. Johnson, Professor, Department of Ceramic Engineering, Iowa State College; Frederick A. Peterson, Professor, Department of Ceramic Engineering, University of Illinois; Frank R. Porter, Inland Steel Company; Edwin M. Rupp, Columbus, Ohio; and William L. Stafford, Mayer China Company.

Following are summarizations of those papers which were made available to THE GLASS INDUSTRY for the purpose:

Surface Tension of the PbO-B_2O_3 and PbO-SiO_2 Systems. *By L. Shartsis, A. W. Smock and S. Spinner, National Bureau of Standards, Washington 25, D.C.*

The compositions investigated were melted in platinum, stirred with a platinum rod and poured into iron molds. Analysis for PbO was made by a triple evaporation with HF and H_2SO_4. The surface tensions were measured by finding the maximum pull exerted on small thin walled platinum cylinder where its lower edge was in contact with the molten glass.





Ralph F. Brenner

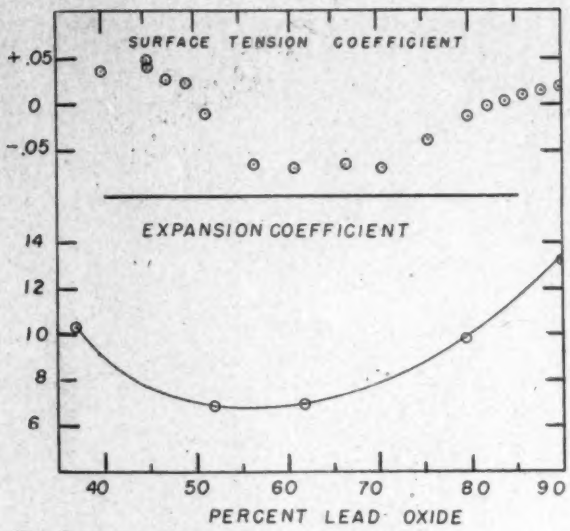


Fig. 2

Figure 1 shows a plot of the data obtained with the PbO-B_2O_3 system at 900°. In the composition region up to 40 per cent PbO the surface tension is almost constant. This is the region where at lower temperatures two immiscible liquids form. The constancy of the surface tension in this region suggests the possibility that the surface may perhaps consist almost totally of B_2O_3.

From about 40 percent PbO the surface tension rises rather steeply to a broad maximum around 84 per cent PbO. In this composition region the Gibbs adsorption isotherm predicts a smaller concentration of PbO in the surface than exists in the main body of the liquid. If the intrinsic volatilities of the two end members are approximately equal, then relatively more B_2O_3 than PbO should be lost upon heating. From 84 to 100 per cent PbO the surface tension drops and, therefore, there is more PbO in the surface than in the main body of the liquid. Heating compositions in the region should cause relatively greater loss of PbO than B_2O_3 and the remaining liquid should become richer in PbO.

Table I shows the effect of heating various glasses in the PbO-B_2O_3 system and verifies the conclusions just made. The actual volatilization loss is given in the last column. The presence of a minimum volatility in the region where maximum surface tension exists is clearly indicated.

Referring to the lower portion of Figure 1 where the temperature coefficient of surface tension is plotted, the two-liquid region is also characterized by almost constant values. Increasing the per cent PbO beyond the two-liquid region causes the coefficient to drop and then become negative. Further increase in PbO causes the coefficient to become less negative until it attains positive values above 82 per cent PbO.

There are theoretical reasons for expecting a parallelism between the coefficient of surface tension and the expansion coefficient. Figure II shows the similarity of the two curves.

Figure III shows a plot of the results obtained with the PbO-SiO_2 system. The upper curve shows the data obtained with the maximum pull method, while the lower curve shows the data obtained by Appen, who used a modified drop weight method. Appen's results are distinctly lower; the difference is to be ascribed to the difference in the methods.

Since the surface tension rises continuously as the percentage of silica is increased, one might expect the volatility to take the opposite course; that is, to decrease as the percentage of silica is increased. This, in general, was found to be the case by Preston and Turner in their important work on volatility of various glass systems.

In lower part of this figure is a plot of the temperature coefficient of surface tension versus composition. The temperature coefficients are all positive and become smaller as the percentage of silica increases. From the parallelism that should exist between the expansion coefficient and the temperature coefficient of surface tension, the expansion coefficient should decrease with increasing silica. Only values in the temperature range from room to a few hundred degrees above are available; but these decrease as the silica increases.

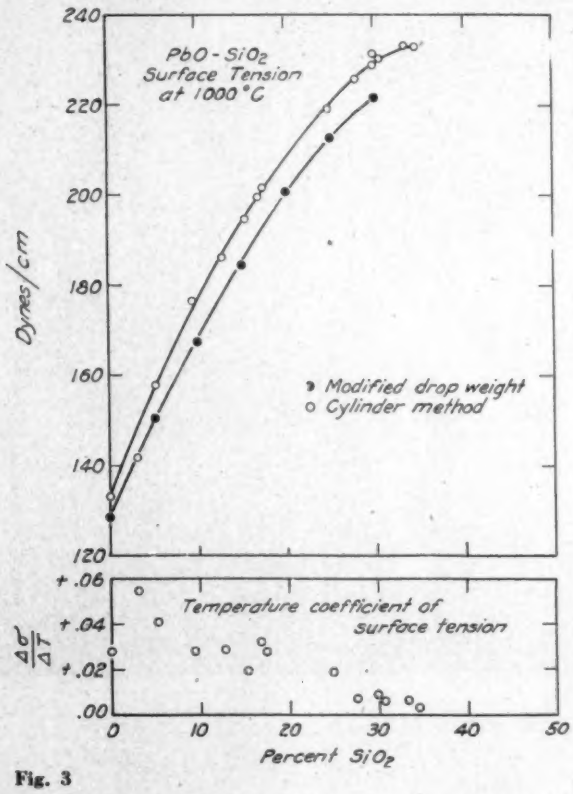


Fig. 3

TABLE I.

Per Cent PbO			Volatilization loss mg/cc
Calculated from batch	Found	After heating	
50.0	51.33	52.91	44*
55.0	56.23*		67
60.0	60.98		60*
65.0	66.50	67.01	50*
70.0	70.70		64*
75.0	75.54	76.48	28*
80.0	79.94	80.40	16*
82.0	82.08	81.21	13*
84.0	84.12*	83.64	13*
86.0	85.97*		
88.0	88.04*	87.92	33*
90.0	89.84*		
92.0	91.91*	91.63	126*

*Average of two determinations

Staining of Glass Containers in Contact with Iron. *By Evelyn C. Marboe and W. A. Weyl, Glass Science, Incorporated, State College, Pa.*

It was observed that in the automatic washing of bottles, wet glass containers which remained in contact with iron for any length of time assumed stains which were difficult to remove even with hydrochloric acid treatments. These stains were reproduced in the laboratory by bringing iron or manganese into contact with the glass while the glass was immersed in water or in aqueous solutions or different salts. The glass composition or its chemical resistivity did not seem to have any bearing on this phenomena, all

glasses, including alkali borosilicates and fused silica, being susceptible to the iron stain.

The fact that the iron must be in contact with glass in order to produce a stain suggested that the explanation of the phenomenon involved a galvanic reaction. A systematic study revealed that iron immersed in water, especially in the presence of minute amounts of chlorides, produces positively charged ions which go into solution. The metal, therefore, becomes negatively charged. A glass surface in contact with the iron acquires a negatively charged halo around the point of contact. This area attracts the positively charged ferric ions into the surface layer where their combination with the silica gel leads to a permanent stain of ferric hydrosilicate.

There are several ways of preventing such staining. All methods which inhibit the corrosion of the iron, such as treatment of its surface with potassium chromate, will prevent stain formation. Another method consists of adding those anions to the water which tend to form anionic complexes with the iron. Small amounts of fluorides, cyanides or calgon (a hexametaphosphate) act in this manner. The reaction of the positively charged iron ions with the glass surface can be prevented also by adding to the solution other positively charged ions, such as Al^{3+} and Cr^{3+}, which in competition with the low concentration of iron ions would have a greater probability of being absorbed in the silica gel. Addition to the water of aluminum chloride or alum, chromium chloride and even hydrogen ions block the active centers in the silica gel and prevent the iron stain.

The fact that a wet glass, even after a very short contact with iron, contains ferric ions on its surface should be considered in all operations where wet glass surfaces are handled. (The stain becomes visible only if the iron layer reaches a thickness necessary to produce Newtonian colors.) The manufacture of optical elements and the preparation of glass for silver coating provide opportunity for such a contamination. Contact with steel parts might lead to the formation of a visible silvery spot. A shorter contact might show up as a breath mark or by producing oily surfaces.

Transmission of Binary Glasses in Near Infrared. *By J. M. Florence, Francis W. Glaze, and C. H. Hahner, National Bureau of Standards, Washington 25, D. C.*

A study has been made of the infrared transmissions of binary glasses. The compositions of the glasses studied are given in Table I. The thicknesses of the samples are also given in the same table.

All the glasses were melted in platinum and the compositions given are those determined by chemical analyses.

The transmissions of representative glasses studied are shown in Figures 4, 5 and 6. The transmission values from which the curves were plotted have not been corrected for

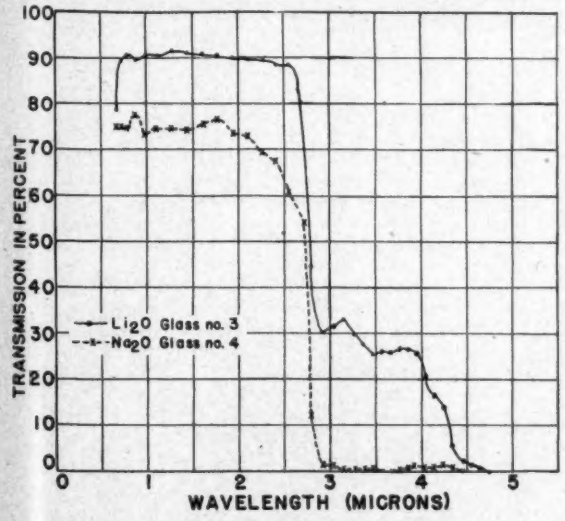


Fig. 4 Comparison of infrared transmission of lithium and sodium silicate experimental glasses.

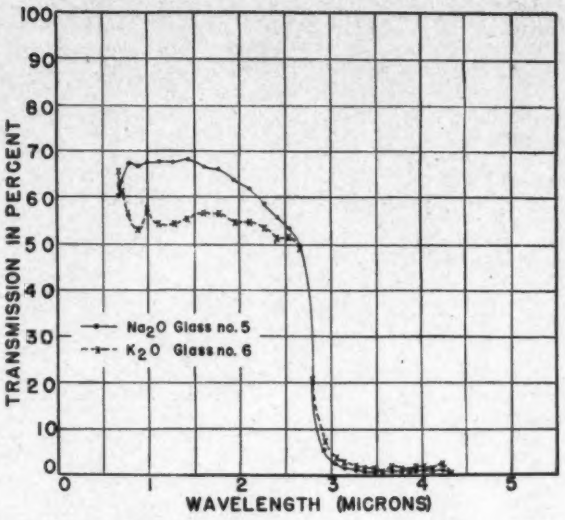


Fig. 5 Comparison of infrared transmission of sodium silicate and potassium silicate experimental glasses.

TABLE I.

Glass Compositions

Glass No.	3		4		5		6	
	Wt. %	Mol. %	Wt. %	Mol. %	Wt. %	Mol. %	Wt. %	Mol. %
SiO_2	80.72	67.56	68.28	68.96	78.01	78.57	71.37	79.63
Li_2O	19.28	32.44						
Na_2O			31.72	31.04	21.99	21.43		
K_2O							28.63	20.37
Thickness mm	5.74		4.67		6.21		4.45	
Glass No.	7		8		9			
	Wt. %	Mol. %	Wt. %	Mol. %	Wt. %	Mol. %		
SiO_2	29.14	60.45	20.09	48.30	11.92	33.46		
PbO	70.86	39.55	79.91	51.70	88.08	66.54		
Thickness mm	3.00		3.21		2.81			

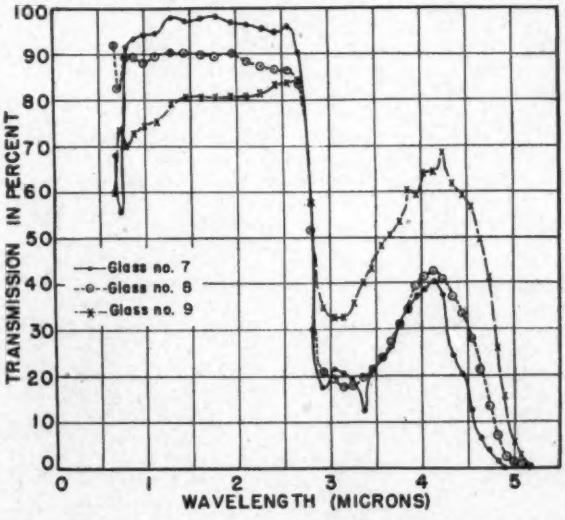


Fig. 6 Infrared transmission lead silicate experimental glasses.

surface reflection and the samples are not of the same thickness (Table I).

It was found that the lithium silicate glass transmits more infrared radiation than the sodium or potassium silicate glasses. Increasing the percentage of lead oxide in a lead silicate glass does not increase the infrared transmission for all wave lengths; however, glass of the composition 71 per cent of lead oxide and 29 per cent of silica will give the maximum infrared transmission in the portion of the spectrum between 0.8 and 2.7 microns. Increasing the lead oxide over 71 per cent will increase the infrared transmission in the region between 3.25 and 5.0 microns, but will decrease the transmission in the region between 0.8 and 2.7 microns.

A Theory of the Mechanism of the Fracture of Glass. *By Nelson W. Taylor, Research Dept., Minnesota Mining & Mfg. Co., St. Paul, Minnesota.*

A very important discovery was made when Preston and Glathart[1] showed that the relation between the stress, f, required to break a glass rod and the duration of application, t, of this stress was given by the empirical expression, $\log t = -a/m + 1/fm$. The quantity m is the slope of the curve when 1/f is plotted versus log t. This means that a high stress applied for a short time will produce fracture, while a slightly lower stress applied for a much longer time to an equivalent specimen will also produce fracture. There are two things that are particularly striking about this equation; one is that it is a linear relation involving reciprocal stress and the other is that it involves not time itself but the logarithm of the time. Preston and Glathart attempted to interpret the quantity 1/f as a measure of the weakness of the specimen, but this concept has not proved particularly fruitful.

It appeared to the writer that the fracture of glass is a rate phenomenon analogous in certain respects to ordinary chemical reaction processes which operate at characteristic rates. It is well known that the prime factor in controlling the rate of such a process (apart from concentrations of reagents) is what is called an activation energy. This activation energy is the minimum energy which a molecular complex must acquire before it is in a position to undergo reaction. Certain atoms must be deformed and certain bonds must be broken or weakened before new bonds can form. We may represent the initial and final conditions of a system which can undergo chemical reaction by two different levels of potential energy, the final level being lower. Both levels may represent reasonably stable situations, i.e., minima in a potential energy diagram, and in order to make the reaction go, the initial system must actually acquire an additional amount of energy which is called the activation energy before it can pass over to the final system. A crude analogy is given by a traveler on a mountain road who passes from one valley to a lower one not by going directly downhill but by climbing first over a pass or saddle-back in the mountain range. The height which he has to climb to reach the summit of this pass may be looked upon as measuring the activation energy. The general rate equation for a molecular process involving an activation energy takes the form: $\text{Rate} = k_o e^{-\text{activation energy}/kT}$. Since the activation energy appears in the exponent in this equation, a small increase in the activation energy produces a very great decrease in the rate. T represents the absolute temperature and k is the Boltzmann constant which is the gas constant R (of the equation $PV = RT$) divided by the Avogadro number N. The constant k_o depends on the dimensions and shape of the specimen, etc. It is the belief of the writer that the slow rate-controlling step which determines the time at which fracture will occur under a given stress f is the slow stretching or elongation of the strong bonds of the specimen, which continues up to a certain limit. When that limit is reached, i.e., when the strongest bond has been stretched by a certain characteristic length, which we shall call λ_o, fracture occurs. In glass λ_o is less than the normal Si-O distance.

Our problem now is to show the relation between the net tension f and the activation energy, and when this relation is obtained it can be substituted in the general rate equation above. In order to get this relation use is made of Hooke's Law, which is usually written in the form: $E = f/(dl/l)$ where E is Young's Modulus, l is the length of the specimen, and dl is the elongation produced by the stress f. This equation may be rearranged in the form: $f/E = dl/l$. We shall now replace the quantity dl/l by the ratio λ_o/r where r is the length of an elementary prism containing an assemblage of atoms which must cooperate to produce the critical elongation λ_o when the stress f is applied. This gives us a measure of r, namely, $r = E\,\lambda_o/f$. It is to be seen that since λ_o and E are characteristic values for the material, r varies inversely with f. If f is large a relatively small number of atoms have to cooperate in order to produce the critical elongation λ_o, and the activation energy will be small. This will lead to a high rate of elongation and a short time for fracture. On the other hand, when f is small r is large, which means that a large number of atoms must cooperate. The activation energy will then be large, the rate will be very small, and the time for fracture will be very long.

Let the cross section of the elementary prism be A and let α be the energy required to activate the atoms in the volume $\lambda_o A$. Then the total activation energy required for all the atoms in the length r is $r\,\alpha/\lambda_o$ or $E\,\alpha/f$. The quantity α depends not only on the nature of the glass itself but also on the environment. It is small when moisture is present. α can therefore not be calculated from the properties of the solid alone but has to be determined from the experimental data. If we substitute the quantity $E\,\alpha/f$ in the general rate equation, we get the expression: Rate of fracture $= k_o e^{-E\alpha/fkT}$. In most fracture experiments in glass, f is only a small fraction of E, usually 1 per cent or less, so that the total elongation is only 1 per cent or less. Hence we have good reason to believe that under a given tension the rate of elongation of the strongest bonds will be constant. We can therefore integrate our theoretical equation in terms of time for fracture as follows: rate is so many events per second; time is so many seconds per event; therefore, *time for fracture* $= 1/$*rate of fracture* $= \dfrac{e^{E\alpha/fkT}}{k_o}$. This expression may be written in the logarithmic form $\log t = -\log k_o + (E\alpha/2.3kT)/f$. This expression is identical in form with the Preston and Glathart equation: $\log t = -a/m + 1/fm$, where $m = 2.3kT/E\alpha$. α can thus be determined exactly from the experimental data since k, T, and the slope m are all known.

As stated above, α depends not only on the nature of the solid but also on the environment. This is borne out by data on several glasses under various conditions and also by certain metals such as brass, whose fatigue rate is very much accelerated by the presence of moisture plus oxygen. Environmental factors such as moisture accelerate the stretching process because such gases are able to react with the atoms of the solid and thereby promote the rearrangement of these atoms. The high strength of glass when tested for a short time and the lesser strength when tested for longer times provide an example of stress corrosion which is no different in principle from the behavior of brittle metals, or rubber in presence of oxygen, and of other materials. The theory advanced here would be applicable not only to glass, porcelain, and the like, but also to other solids.

A comment should be made about the nature of the elongation process. When tension is applied to a piece of glass there is an immediate stretching which may or may not be followed by a small additional stretching. I believe that the initial stretching is carried by the weaker bonds of the system, and that with the passage of time there is a transfer of some of this strain from the weaker bonds to the stronger ones so that the latter becomes stretched, but this may occur without any additional increase in length. Actually if f/E were no greater than 1 per cent the total stretch would be no greater than this amount. However, if the load is left on for a period of time a little less than the period needed to produce fracture, and then removed, the sample should be slightly deformed and should not return exactly to its original condition immediately but would do so after a period of time. This phenomenon of the delayed elastic effect is a well known property of glass as well as of other solids and is illustrated in the case of glass by the slow drift of the ice point of a thermometer which has been held at room temperature. Another well known example is the decline in pitch of a violin string held at given length.

Headed for the Glass Division Meetings at the Auditorium

F. R. Matson

Evelyn C. Marboe

S. R. Scholes

K. C. Lyon

Dr. and Mrs. F. W. Preston and E. W. Summers

A. E. Badger

V. H. Remington

Rudolpho L. Garcia, P. S. Montemayor, M. Garza and A. F. Rodriquez

E. L. Hettinger and Louis Navias

Aaron K. Lyle

D. E. Sharp and J. C. Hostetter

H. Mcre and B. Delgado

M. H. Picard and H. H. Blau

The theory as outlined indicates the very great importance of the environment and shows why attempts should be made either to develop glasses which are unaffected by moisture or to protect the surface of these glasses (as soon as they are formed) against moisture or other corrosive agents. In one experiment brought to my attention a piece of glass *in vacuo* was subjected to load of 50,000 p.s.i. and held so for several weeks without fracture. A stopcock was then opened admitting ordinary air (at normal humidity) to the system. The piece broke immediately. Parallel phenomena have been observed with metals. It is well known to the wire industry that a brass wire supporting a picture is likely to break and fall when the housewife cleans the room with ammonia. This has been a common occurrence. Other examples may occur to the reader.

A more comprehensive treatment of the mechanism of fracture will be published elsewhere.

REFERENCE

1. J. L. Glathart and F. W. Preston, "The Fatigue Modulus of Glass"; Jour. Appl. Physics *17*, 189-195 (1946); see also F. W. Preston, "Strength of Glass and Duration of Stressing," Nature *156*, 55 (July 14) 1945.

The Effect of Chemical Composition on the Durability of Bottle Glass. *By H. E. Simpson, Department of Glass Technology, New York State College of Ceramics, Alfred, N. Y. (formerly of Mellon Institute, Pittsburgh 13, Pa.).*

The chemical durability of glass is a subject of extreme importance to all manufacturers of glass products and the development of glasses that are resistant to attack by moisture, alkalies and acids is one of the main problems of glass technology. A study of the various methods used for testing the durability of glass revealed that no single method was completely satisfactory, nor did any one method fully evaluate the "overall resistance" of a glass.

In this study, a number of container glasses—a pressed ware glass and a borosilicate glass—were compared by testing the glass surfaces as received for resistance to attack by moisture, acids and alkalis. Attack by acid was measured by loss in weight in constant boiling hydrochloric acid and resistance to alkali was measured by loss in weight in 2N caustic soda solution. Attack by moisture was studied by exposing glass to high humidity (approximately 100 per cent) at an elevated temperature (50° C.) for 30 days and observing the resulting surface deterioration. This humidity test when operated so as to maintain uniform temperature throughout the humidity chamber appeared to give results that lead to a relative comparison between glasses.

While the glasses used did not follow a planned series but represented a group of commercial composition, certain breakdowns of constituents and their influence was possible. A comparison of test results with such a general segregation of glass types led to the following conclusions: 1) Al_2O_3 gives definite resistance to moisture attack (the glasses studied contained up to 3.5 per cent Al_2O_3); 2) B_2O_3 contributes resistance to attack by moisture; 3) no great difference in weathering tendency was noticed from inside to outside of bottle; 4) borosilicate glass was high in its resistance to attack by water and acid, but low in alkali resistance; 5) bottle glass low in soda (14.8 per cent) was good in its resistance to acid and alkali but poor in its resistance to high humidity.

The Functions of the Minor Constituents in the Commercial Selenium-Ruby Batch. *By R. R. Shively, Jr. and W. A. Weyl, Glass Science, Incorporated, State College, Pa.*

The purpose of this study was to start with a formula of a commercial selenium ruby glass and to examine the roles which several of the minor, but essential, constituents play in its production. In addition, an attempt was made to describe the function of each constituent in terms of the present picture of the constitution of glass. The particular formula chosen contained silica, soda, potash, boron, zinc oxide, cryolite and bone ash, in addition to the colorants, selenium and cadmium sulphide. A small amount of sodium chloride was used as a non-oxidizing fining agent in this formula.

In the study of the role of ZnO, a series of selenium ruby glasses were melted on a laboratory scale and the zinc oxide was gradually replaced by calcium oxide on a weight per cent basis. This replacement was found to decrease the color intensity to such an extent that the pure calcium end member was practically colorless. In addition, it was found that as the zinc content increased, the amount of selenium retained in the glass increased. Zinc also lowered the melting-temperature.

The role of cryolite (fluorine source) in this particular formula was found to 1) improve meltability of the glass; 2) increase the low temperature mobility of the glass forming units, thus increasing the rate of striking; and 3) increase the number of color centers by lowering the equilibrium temperature of the glass.

The addition of bone ash, especially in combination with additional fluorides, produces crystal nuclei of apatite which in concentrations still insufficient to produce actual capacity provide seeds for precipitation of the colorant (cadmium sulfoselenide).

The presence of traces of copper and nickel compounds in the selenium ruby batch produce crystal nuclei on working out the glass so that during a normal operation the color strikes without requiring a special heat treatment. Some of the raw material used in the manufacture of this type of glass often contain a sufficient concentration of heavy metals to influence the striking properties. This explains the reason why sometimes a change, even to a better grade of material, might lead to difficulties in striking.

In the discussion on the nature of the colorant, it was shown that the glass batch must contain the three elements, cadmium, sulfur and selenium, if the selenium ruby color is to be produced. While sulphur may not be added as such, it nevertheless is present as an impurity in the raw materials or by reduction from sulphates. Since the color is due to a compound whose solubility limit in the glass has to be exceeded, it is not possible to "dilute" a selenium ruby at will.

Alkali sulfoferrite and selenoferrite produce a red-brown color, and their formation in glasses by the means of strong reducing agents, accounts for the deep color of some glasses containing only small amounts of cadmium sulfoselenide.

A New Interpretation of Certain Discontinuities in Property-Temperature Curves for Glasses. *By W. R. Ham, A. G. Pincus and C. H. Samans, Research Laboratory, American Optical Company, Southbridge, Mass.*

Many previous investigators of glasses have found discontinuities in property-temperature curves, but because no one was able to offer a rational explanation, the validity of their results has been frequently questioned. The objective of this paper was to offer a new interpretation of these breaks which the authors refer to as "thermal series transitions" or, more simply, as "series transitions," and to show that they are genuine and characteristic of the chemical elements of which the glass is composed. The authors state that no effort will be made at this time to give a physical explanation for the phenomena because thus far it has not been possible to fit the facts into current theories of condensed states.

The physical property used in this investigation was that of electrolytic conductance. Measurements of electrolytic conductance were made at small intervals over a consid-

Table I

Tentative Thermal Series Transition Constants for Some Elements in Condensed States

Atomic Number	Element	$n_o = 1$ ct	$n_o = 1$ T∞	$n_o = 2$ ct	$n_o = 2$ T∞	$n_o = 3$ ct	$n_o = 3$ T∞	$n_o = 4$ ct	$n_o = 4$ T∞	$n_o = 5$ ct	$n_o = 5$ T∞
8	Oxygen	532	532	2660	665	5320	591	5320	332		
11	Sodium	746	746	3730	933	5595	622	5595	350		
12	Magnesium	1044	1044	5220	1305	9400	1044				
14	Silicon	780	780	3900	975	7800	867	11690	731	11690	468
17	Chlorine	874	874	4370	1092	7870	874				
19	Potassium	1084	1084	5420	1355	9760	1084	12460	779		
20	Calcium	980	980	4900	1225	8820	980	12730	796		
26	Iron	1064	1064	5320	1330	12500	1389	17024	1065	17024	681
28	Nickel	756	756	3780	946	8890	988	12820	802		

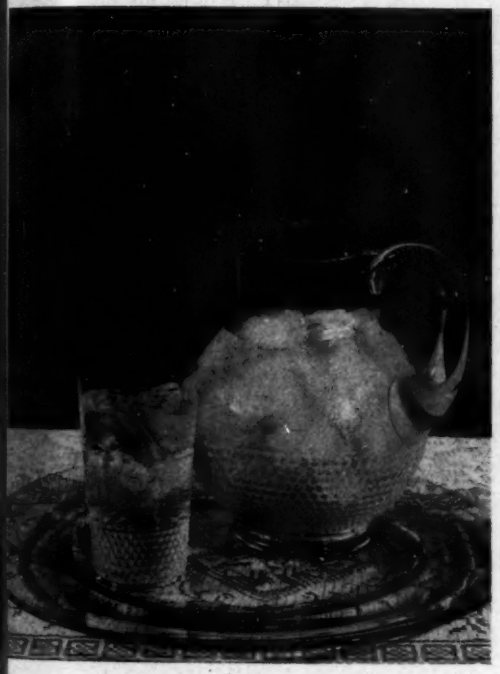
(*Continued on page* 312)

"Currier and Ives" by Rolland Roup
First Prize, Pictorial

"The Old Canal" by E. L. Hettinger
Second Prize, Pictorial

Prize Winners 1947

Ceramic Camera Club

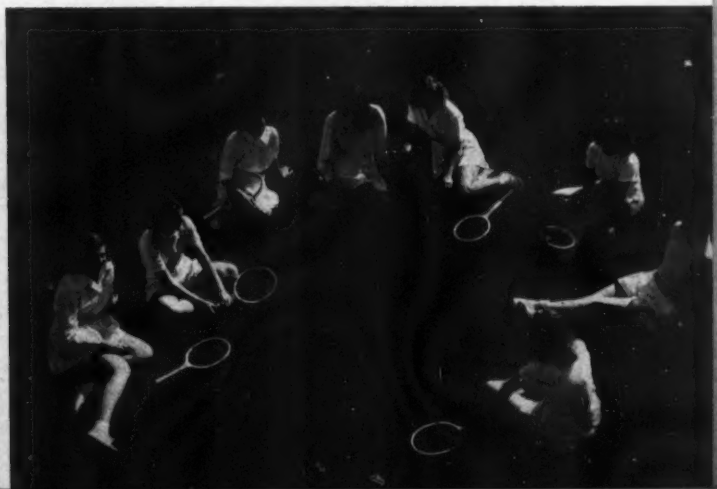


"Cold Water" by V. H. Remington
F. J. Vontury Award and
Chauncey E. Frazier Award

"The Beauty of Winter" by Rolland Roup
First Prize, Portrait

"Hopalong and Roy" by J. Earl Frazier
Second Prize, Portrait

"Tennis Circle" by Donald P. Falconer
Third Prize, Pictorial



SOME PRACTICAL ASPECTS OF THE SURFACE CHEMISTRY OF GLASS

By W. A. WEYL*

PART II

IV. Structural Changes of the Glass Surface and Their Technical Implications

(*1.*) *Molecular rearrangements due to surface and interfacial tension.* A given number of positive and negative ions will arrange in such a way that the free energy of the system reaches a minimum. This is achieved by forming a geometrical pattern yielding maximum attraction and minimum repulsion. Each ion surrounds itself with ions of the opposite charge or, in the parlance of the chemist, each ion tries to come as close as possible to the one for which it exerts the greatest chemical affinity and as far away as possible from the next one of its own kind. For simple systems containing only two types of ions, such as NaCl, one can calculate the energy gained through the formation of the crystal lattice, especially if it has a high symmetry. The stability of the system is greatest if the geometrical pattern provides the maximum lattice energy. It can be easily shown that a stable arrangement should have a small surface area and not form a thin film because ions participating in the surface area cannot contribute as much to the lattice energy as those in the interior. Because of its greater surface, a finely powdered material or a film of substance a few molecules thick has a higher energy content and is less stable than the same quantity of the substance in the form of large crystals. A fine powder, therefore, has a tendency to decrease its surface free energy through recrystallization just as a liquid free of external forces decreases its surface by assuming the shape of a sphere which has the smallest surface for a given volume. For the same reasons a silver mirror will crack and recrystallize if thermal motion of the silver atoms permits such rearrangement on the glass surface. According to T. Liepus,[18] recrystallization of a silver mirror on glass begins at 250°C in the presence of oxygen.

Liquids containing several types of molecules have an additional way to decrease their surface free energy, namely, by bringing to the surface those molecules which exert the least attraction for the rest of the group. Molecules of this type are called "capillary active" or "surface active". They are also called "wetting agents" due to the fact that their presence in water makes it easier to increase its surface and wet the surface of a solid.

At the present time, Glass Science is engaged in research on the role of capillary active constituents in fused salts in general and glasses in particular. Little is known about this subject but the phenomena are of great interest to glass technologists.

Surface forces in relation to glass technology are usually associated with their influence on the shape of blown glass, the rounding of edges of tumblers and the smoothing of a surface through fire polishing. These phenomena, however, are caused by only one of the manifestations of the surface free energy of glass, namely, the assumption of the shape with the minimum surface area.

It is customary to explain this property by a tension existing in the surface layer of liquids. Liquids are described as being surrounded by a skin under tension, causing them to behave as though enclosed in a rubber bag. Indeed, many phenomena can be explained on this basis and the trick of making a slightly oiled steel needle swim on the surface of water seems to provide visible evidence of the existence of a surface skin.

In the literature pertaining to surface phenomena of glasses, one finds scarcely any reference to the true cause of these phenomena, the above mentioned energy relations, but finds the surface tension described as a force per unit length acting in the surface. Accordingly, the surface tension of glasses is expressed in dynes per centimeter.

This picture, however, is too simple for the understanding of many phenomena involving surface free energy. It is likely that this narrow concept must be blamed for the delay in progress in the understanding of wetting, adhesion and other problems involving surface forces. The limitations imposed on a scientist by his thinking of matter as a "continuum" may be negligible in certain problems but may become a handicap in others.

N. K. Adam[19] in his authoritative book on "The Physics and Chemistry of Surfaces" describes the situation very aptly as follows:

"This free energy in the surface is of fundamental importance; a vast number of problems relating to the equilibrium of surfaces can be solved without knowing more than the magnitude of this free energy. In the solution of such problems a mathematical device is almost invariably employed to simplify the calculations; it is to substitute for the surface free energy a hypothetical tension, acting in all directions parallel to the surface, equal to the free surface energy. This is what is generally known as the "surface tension". It is always possible, mathematically, to replace a free energy per unit area of surface by a tension acting parallel to the surface. Such a surface tension has, of course, the same dimensions as a surface energy mass $\times$ time^{-2}; and it must have the same numerical magnitude. The work done in extending a surface which is pulling with a tension τ dynes per cm., by one square cm., will be τ ergs per sq. cm.: hence the free surface energy of such a surface will be τ ergs per sq. cm.

"The great convenience of the hypothesis of surface tension, as the equivalent of free surface energy, combined with the fact that it was in use nearly a century

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before the conception of energy became definite, has given the words 'surface tension' a predominance in the literature of surfaces, which does not rightly or logically belong to them. The term 'surface tension' has often been strained to imply that liquids have in their surfaces some mechanism like a stretched membrane pulling parallel to the surface. The surface is said to be in a 'state of tension'. This view must not be pushed too far. Any mechanism possessing free energy in the surface will undergo the spontaneous contraction which has led to the idea of surface tension; hence we can gain practically no idea of the actual nature of the mechanisms in the surface from this fact of spontaneous contraction alone. The view that there is some skin in the surface, pulling parallel to it, leads to great difficulties when the structure of the supposed skin is considered in terms of molecules."

When discussing the structure of glass, we divided the cations into two groups, network-formers and network-modifiers, a classification which is based on the strength of their electric fields. The monovalent and relatively large Na^+ and K^+ exert a much weaker attraction on the anions than the small and four fold-positive silicon ions. Silicon ions will always try to completely surround themselves with oxygen ions and form the stable anionic groups, SiO_4^{4-}. Si^{4+} ions, therefore, are not likely to be found in the surface. Silicon ions with incomplete coordination are improbable because they would raise the free surface energy of the glass to an extremely high value. Boron, on the other hand, is known to participate in the glass structure as BO_4^{5-} as well as BO_3^{3-} groups. The energy difference between these two groups must, therefore, be small and, as a result, boron is likely to go into the surface in the form of the triangular BO_3 grouping. The fact that boric oxide enters the surface layer might very well account for its effect on the appearance of the glassware. Even minor additions of boric oxide to the batch are claimed to increase considerably the gloss of its surface, thus improving the appearance of the ware.

Alkali ions also lower the surface tension of a glass, as can be seen from Table II, which, according to K. C. Lyon,[20] expresses the effect of 1 per cent of glass constituents on the surface tension of a sodium silicate glass whose SiO_2:Na_2O ratio exceeds 3.25.

TABLE II

Oxide	Effect on Surface Tension in Dynes/cm. 1200°C	1400°C
SiO_2	3.25	3.24
Al_2O_3	5.98	5.85
B_2O_3	0.23	–0.23
CaO	4.92	4.92
MgO	5.77	5.49
BaO	(3.7)	(3.8)
Na_2O	1.27	1.12
K_2O	(0.0)	(–0.75)

The values for BaO and K_2O give only the order of magnitude.

From this table, it is evident that B_2O_3 and the alkalies, K_2O more so than Na_2O, migrate to the surface. This explains the previously mentioned phenomenon, namely, that at elevated temperatures the insulating power in vacuo even of low alkali glasses deteriorates gradually.

The surface tension of a glass is responsible for its assuming a shape with the smallest surface area, a sphere in case there are no other forces acting upon it. In addition, surface tension brings those constituents into the surface layer which decrease the surface free energy (alkali, boric oxide). This explains why even minor additions of alkali (such as in the low alkali borosilicate glasses and certain fiber glass compositions) influence surface properties if the glass is kept for any length of time at elevated temperatures or subjected to heating cycles. The beneficial influence of boric oxide on the appearance of glassware can be explained on the same basis.

In these cases when speaking of the surface, we refer to the glass-air or glass-vacuum interface. The molecules in a gas are so far apart that they cannot exert strong forces upon the glass surface and, as a result, their influence is negligible. This, however, is not true if we consider glass-liquid or glass-solid interfaces. The interfacial tension, in this case, depends to a great extent on the nature of the adjoining phase. The composition and structure of a glass surface adjoining a metal or a refractory oxide must, therefore, be different from that adjoining the air.

Phenomena concerning interfacial tension are of great practical importance in the technology of glass and in related fields. A fraction of one per cent of tin oxide in a glass influences the aggregation of gold during the striking of gold ruby. Assuming a statistical distribution of tin ions in the glass, such an effect could scarcely be explained. The forces which exist between metals and those ions which have an incomplete outer electronic shell are responsible for the solubility of metals (Au, Ag, Cu) in glasses containing Pb^{2+}, Sn^{4+}, Ti^{4+}, Bi^{3+}, or Sb^{5+}.

The specific forces acting between ions of this type and metals cause "metallophilic" ions to migrate into the glass-metal interface. The adhesion of cobalt or molybdenum containing enamels on steel requires that these minor constituents migrate into the glass layer adjoining the metal phase. It is not possible for 0.5 per cent cobalt oxide to exert a profound influence on the wetting and adhesion if the Co^{2+} ions are statistically distributed in the ground enamel. A similar molecular rearrangement seems to account for the phenomenon that small amounts of sulfide ions improve the wetting qualities of steel by enamel. Only by assuming extraordinary strong forces acting between the adhesion promoting ions and steel could one explain why the minute concentrations of cobalt ions cause an enamel to adhere or why the replacement of an occasional O^{2-} by an S^{2-} increases wetting of a steel surface by glasses. The reverse phenomenon, however, namely the existence of substances such as iodides which in minute quantities prevent the normal wetting of platinum by glass, provides conclusive evidence for the migration of these "capillary active" substances into the glass-metal interface. Low melting borate glasses which ordinarily adhere to a platinum crucible will not adhere if minute quantities of heavy metal iodides (AgI or BiI_3) are added.

The behavior of fused salts to a glass surface (wetting or non-wetting) involves similar phenomena. Melting sodium or potassium chloride in a glass or glazed por-

celain crucible produces strong adhesion. After cooling, the melt cannot be removed easily. The same applies to fused sodium or potassium iodide. However, if minute amounts of an iodide have been added to the alkali chloride melt, the latter will no longer adhere to the glass or glaze or to the platinum of a crucible. Slight tapping of the crucible causes the used salt to fall out in one piece.

E. C. Marboe and the author have studied the conditions which cause some salts to adhere to glass or to platinum and others not. As will be pointed out in a later publication, for those cases where no chemical corrosion takes place, it is possible to predict from the chemical formula of a simple inorganic compound whether or not it will adhere to platinum or glass.

Interfacial forces are responsible for adhesion and wetting, as pointed out for enamels and gold ruby glass. Similar forces come into play if a glass is in contact with refractory oxides. If pure aluminum oxide in the form of "sinter corundum" is used as a crucible for glass melting, the glass melt often can be removed easily in one piece by tapping the bottom of the crucible with a mallet. There seems to be no strong attraction between a silicate glass and well crystallized Al_2O_3. The same is true for platinum and gold if the glass consists only of ions having electronic structure of rare gas (Si^{4+}, Na^{+}, Ca^{2+}, O^{2-}). In vacuo neither platinum nor gold will be wet by a fused sodium silicate.

I. Sawai and M. Mine[21] investigated the suitability of various materials for bushings to be used for the manufacture of fiber glass. They found that orifices made of sinter corundum or platinum will allow twice the volume of glass to flow through as an orifice made of fire clay. In the temperature range between 1000 and 1100°C, where corrosion is still negligible, the forces between the fused glass and the fire clay are strong enough to delay its flow.

TABLE III

Temperature of Glass	1000°	1050°	1100°	1150°
Glass flown through orifice made of platinum or Al_2O_3	0.04	0.09	0.16	0.26 g/min.
Glass flown through similar orifice made of fire clay	0.02	0.04	0.08	0.04 g/min.

The interfacial tensions between two glasses of different compositions are important factors governing the homogenizing of cords which reach the glass surface. H. Jebsen-Marwedel[22] in several papers pointed out the importance of surface tension forces for the process of homogenizing glass. His experiments are convincing and his results have been corroborated by W. B. Silverman.[23] There can be no doubt that among the various manifestations of interfacial forces in glass technology their role in homogenizing glass is of greatest practical importance. A cord whose surface tension is lower than that of the bulk of the glass will spread out to a thin film once it reaches the surface of the melt. This thin film envelopes the bulk of the glass and finally disappears through diffusion.

M. A. Knight[24] pointed out that the role of surface tension in the process of homogenizing glass should not be overrated. The interfacial tension existing between the bulk of the glass and a completely immersed cord is zero or negative because there can be no positive interfacial tension between two miscible liquids.

Here is a typical example for the previous statement that the use of the term surface or interfacial tension imposes serious limitations on the explanation of many phenomena. The forces acting between the lead oxide of a jewelry enamel and its supporting gold foil can be discussed on the basis of "interfacial tension." The same forces make a heavy lead glass a good "solvent" for metallic gold and thus a gold ruby can form. Here, however, specific solvent forces have to take over the role of the interfacial tension because the gold is no longer a continuum.

2). *Volatility of glass constituents.* The mechanization of glass manufacture, especially the introduction of the Fourcault and Danner processes for draw-glass into the form sheets and tubes, called for glass compositions whose upper limits of devitrification were higher than those used for hand blowing operations. With the introduction of these machines, glass technologists all over the world began to study the devitrification of soda-lime glasses and their modifications through alumina and magnesia. The ternary diagram Na_2O-CaO-SiO_2 has been worked out by G. W. Morey and N. L. Bowen.[25] On first thought, one might expect that this diagram contains the information which is needed to understand and prevent devitrification. The phase diagram gives the liquidus temperature, that is, the highest temperature at which the melt of a given composition is in equilibrium with its primary crystalline phase. Above the liquidus temperature the melt cannot crystallize. However, a considerable discrepancy has been found to exist between the teachings of phase diagrams and the experience of the glass melter. For example, a melt containing 74% SiO_2, 8% CaO and 18% Na_2O has a liquidus temperature of 925°C but its upper limit of devitrification, according to W. Mullensiefen and E. Zschimmer,[26] is about 100°C higher. Why can the phase diagram not be applied directly to this practical problem? In order to answer this question, we have to know that the composition of the glass surface undergoes a change because of the volatility of the alkali. The removal of alkali in turn raises the liquidus temperature sharply, as can be seen from the phase diagram by moving from the point representing the glass composition in the direction away from Na_2O. Volatility of the alkali explains why devitrifications in the surface layer are more frequent than those in the interior of the glass.

With highly opacified fluoride glasses, the opposite phenomenon can be observed. Here the volatility of the alkali fluoride changes the composition of the glass surface in a way which decreases or even prevents opacification. Since these glasses are rather fluid, convection currents often draw the non-opacifying skin into the interior of the glass melt with the result that on working out or pouring, the opal glass shows a complicated pattern of "watery streaks."

3). *Base exchange reactions of the dry glass surface.* Over a wide temperature range, glasses behave like rigid solids. Several phenomena, however, indicate that the alkali ions have a considerable mobility and are able to migrate through the mechanically rigid framework. The

(*Continued on page* 324)

INVENTIONS AND INVENTORS

A Summary of Recently Issued Patents of Interest to the Glass Industry

Feeding and Forming

Jeannette Glass Company Method of Pressing, Fig. 1. Patent No. 2,419,763. This patent is an invention by Robert P. Cassell and it discloses a new method of pressing articles such as drinking mugs. The method is adapted for the manufacture of any kind of pressed containers having heavy bottoms. The basic feature of the invention rests on the discovery that the bottom plate of a press mold may be withdrawn after the first pressing to permit some cooling of the bottom without destroying the shape of the pressed article and the bottom plate may then be replaced to correct any slight deformation of the ware.

Fig. 1 shows the sequence of the steps in the pressing operation which would ordinarily take place on a rotary table. A table 1 carries a series of split molds 2 having bottom portions 3. A plunger 8 has a head 9 arranged to be projected into the mold cavity and to be lowered therefrom by a cam track 12 a, b, c, etc.

At station A, a charge of glass is delivered to the mold while the plunger head 9 is in elevated position. The mold then moves to station B where the press plunger 15 descends to press the ware and is then immediately withdrawn. The mold then moves to station C where the plunger head 9 is lowered so as to permit air from the chamber 6 to be discharged against the bottom of the ware. This cools the heavy bottom while allowing little or no sagging. As the mold moves to station D, the plunger head 9 (which has cooled somewhat) is lifted to its original position which restores the ware to its original shape in case it has been slightly deformed. As the mold passes to station E, the bottom plunger 9 is again lowered so as to permit final cooling of the bottom by air from the chamber 6.

The following references are of record in the file of this patent: United States Patents 2,350,220, Ehret, Jr., May 30, 1944; 1,471,608, Irwin et al., Oct. 23, 1923; 858,812, Johns, July 2, 1907; 994,806, Wanko, June 13, 1911; 162,791, Beck, May 4, 1875; and 1,680,544, Ingle, Aug. 14, 1928.

Jeannette Glass Company, Reflector Button Press, Fig 2. Patent No. 2,419,764. This patent is also an invention by Robert P. Cassell who assigned it to the Jeannette Glass Company. The patent shows a machine for carrying out a new method of pressing reflector buttons as used in highway markers although the same method may be used in the manufacture of other articles of similar character. As is well known, such buttons usually have a central annular flange with projections of smaller diameter on each side. The specification states that great difficulty has been encountered in molding such articles automatically and, therefore, they have usually been made of the larger diameter for the full length and then ground to provide the central flange.

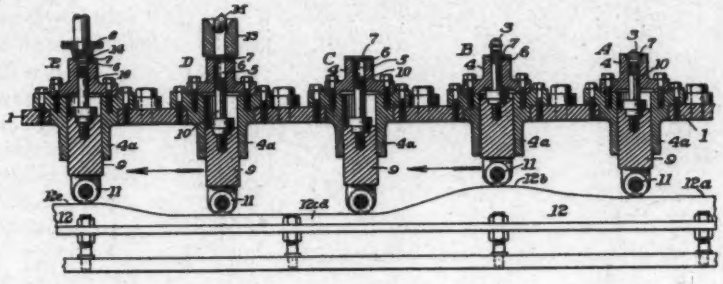


Fig. 2. Jeannette Glass Company Reflector Button Press.

The machine is described as of the turret type in which 12 mold heads are advanced step by step. Fig. 2 is a section through five of these heads which move from right to left as shown by the arrows. At station A, a reflector button 3 is seen in mold 4 which is in the last position of a series of cooling stations. The mold has a cavity 5 which is enlarged at 6 to form the flange on the button. The mold has a base 4a projecting below the table 1 and this base carries a sliding stem 9 having a bottom plunger 10 extending into the mold cavity. A roll 11 on the bottom of the stem 9 rides on a cam-track 12 which causes the bottom plunger to be moved up and down as the table advances. At station A, the portion 12a of the cam-track holds the bottom plunger 10 in pressing position where it supports the cooled button 3.

As the mold approaches station B, a rise 12b on the track raises the bottom plunger 10 to lift the button above the mold so that it can be taken out easily. At station C, the empty mold is cooling and a section of 12cd of the cam-track has lowered the bottom plunger 10 so as to increase the size of the mold cavity. At station D, a mold charge M is delivered to the mold through a funnel 13. The bottom plunger is still in lowered position so that the mold charge will drop down below the top of the mold 10. The pressing operation takes place at station E. As the mold approaches this station, a section 12e of the cam-track lifts the bottom plunger 10 and, at the same time, a top plunger 8 descends until its nose

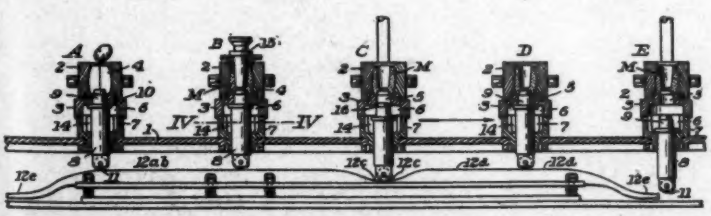


Fig. 1. Jeannette Glass Company Method of Pressing.

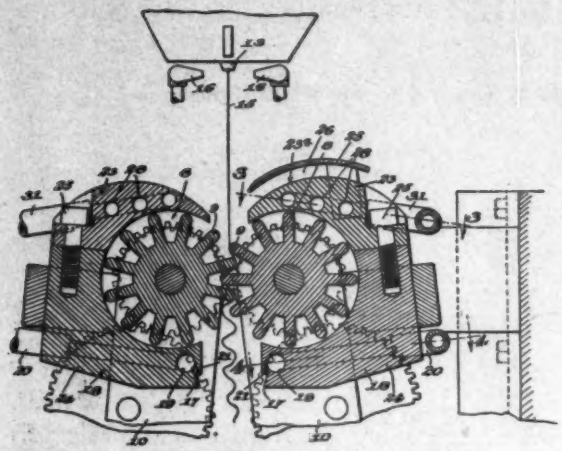


Fig. 3. Owens-Corning Fiberglas Crimping Machine.

14 seats in a recess 7 in the top of the mold. In this way, the button is pressed by the plunger 8 at the instant the mold comes to rest. The top plunger is then lifted and the button cools until it reaches station B.

The following references are of record in the file of this patent: United States Patents 810,570, Sages, Jan. 23, 1906, and 2,233,057, Luce, Feb. 25, 1941. Foreign Patent 501,865, British, Mar. 7, 1939.

Glass Compositions

Pittsburgh Plate Glass Company Glass Composition. Patent No. 2,419,302. This patent relates to optical glass containing large amounts of lead oxide. The invention provides a dense flint glass in which the characteristic yellow color is eliminated. The patent was assigned to the above company by Harry A. Truby of New Kensington, Pa.

Flint glass as understood in the optical field is divided into three groups in accordance with their lead oxide content, these being called light, medium and dense flint. Dense flint is usually accepted as those glasses containing over 45 per cent by weight of lead oxide. Such dense flint glass has always an objectionable yellow color. Mr. Truby has found that the addition of from about 0.1 to 1.5 per cent by weight of sodium sulphate to the batch will remove the objectionable color of the glass.

The following table gives three typical compositions of batches which will produce colorless dense flint glass, these compositions being, of course, subject to variation:

	I	II	III
	Per cent	*Per cent*	*Per cent*
SiO_2	36.50	37.50	38.50
PbO	53.40	51.25	49.55
K_2O	4.85	5.88	6.49
Na_2O	1.06	1.25	1.42
TiO_2	3.47	3.44	3.40
As_2O_5	.36	.34	.32
Na_2SO_4	.36	.34	.32

The following references are of record in the file of this patents: United States Patents 1,166,922, Mears, Jan. 4, 1916 and 1,287,005, Handy, Dec. 10, 1918. Foreign Patents, 1,195, British, 1880 and 15,743, British, 1885.

Glass Wool and Fiber

Owens-Corning Fiberglas Crimping Machine, Fig. 3. Patent No. 2,418,873. This patent is on a machine for by Ed Fletcher of Newark, Ohio, and Henry Snow of attenuating and crimping glass fibers. It is an invention Lonsdale, R. I., who assigned it to the above company.

Patent No. 2,230,272 to Slayter shows a method of making fibers by flowing a stream of glass between the teeth of intermeshing gears which rotate at high speed. If crimped fiber is desired, the temperature of the glass is such that it solidifies with the crimp in it. It was difficult to obtain long length fibers by this method.

The invention overcomes this objection by blowing air on the fiber in the direction of its movement, thereby permitting greater attenuation which results in fibers of greater length. Mechanism is provided to control all air currents in the vicinity of the crimping rolls.

As shown in Fig. 3, gears 8 have intermeshing teeth 9. The gears are mounted on pivoted arms 10 so that the gears may be moved toward and from each other while the teeth 9 remain out of contact. A stream of glass 15 flows from a feeder 13 in the general manner shown in Patent No. 2,165,318 to Thomas and Fletcher. Blowers 16 may be provided to regulate the temperature of the stream as shown in Patent No. 2,291,289 to Slayter and Thomas. The gears 8 attenuate the fiber and crimp it, but whether the crimp remains in the finished fiber depends upon the temperature of the glass.

In order that the fiber may not be broken by the resistance of the air as it leaves the gears 8, blowers 17 are provided in the shields 18 which are connected with compressed air by means of chambers 19. The blower nozzles 21 direct a blast of air onto two sides of the fiber in the general direction in which it is moving. By varying the air pressure, the size of the crimps may be varied.

Any air that may be pumped upwardly by the gears is prevented from acting on the glass stream 15 by the nonsymmetrical arrangement of upper shields 23 and 23a and by a baffle 25. The feature of this invention which relates to controlling the air currents adjacent to the attenuated fiber may be used to advantage in the manufacture of other plastic fibers such as "nylon", etc.

The following references are of record in the file of this patent: United States Patents 2,133,236, Slayter et al., Oct. 11, 1938; 2,206,060, Slayter, July 2, 1940; 2,230,272, Slayter, Feb. 4, 1941; 2,206,058, Slayter et al.,

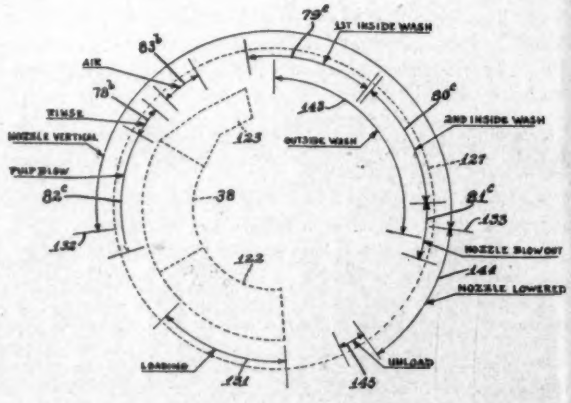


Fig. 4. Owens Machine for Emptying and Washing Bottles.

July 2, 1940; 2,225,667, Staelin, Dec. 24, 1940; and 1,968,693, Kroger et al., July 31, 1934.

Miscellaneous Processes

Owens-Illinois Machine for Emptying and Washing Bottles, Fig. 4. Patent No. 2,418,691. This patent is an invention by Olav Bjering and Robert K. Belnap, Jr., who assigned it to Owens-Illinois Glass Company. The invention is illustrated as adapted to the use of emptying tomato pulp from bottles or other containers and then washing the bottles. Apparently, the machine is not intended for table use, but it would seem that the emptying feature might be applied to some catsup bottles sometimes found in restaurants.

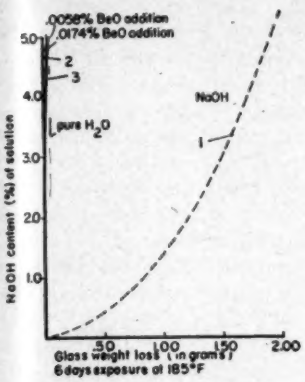


Fig. 5. Improved Method of Washing Glassware.

The machine comprises a turret having 16 heads which rotate continuously in a clockwise direction. Fig. 4 is a chart showing the various operations performed on the bottle as it travels. The operator places the bottles on cradles at a loading station shown at 131 where the bottle slides down so that a nozzle projects into the bottle. The bottle at this time is in an angular position. As it reaches the line 132, the bottle and nozzle are turned to a position where the bottle is vertical with its neck down. Air is then admitted through the nozzle to expel the pulp (marked "pulp blow" in the drawing) and then the bottle is rinsed with water. Then air is again blown into the bottle at 83b to complete the emptying of the bottle.

At 79c, water is again forced into the bottle to wash it. The water is cut off for a brief interval and this is admitted again at 80c to wash the inside for a second time. At 81c, air is admitted to blow the remaining water out of the bottle. The arc 143 indicates the time during which the outside of the bottle is also washed. During the arc 144, the nozzle is retracted from the bottle and at 145, the cradle swings down so that the clean bottle slides onto a discharge chute.

The following references are of record in the file of this patent: United States Patents 2,115,202, Kimball, Apr. 26, 1938; 2,115,204, Kimball, Apr. 26, 1938; 555,598, Donally, Mar. 3, 1896; 755,018, Laible, Mar. 22, 1904; 736,769, Parker, Aug. 18, 1903; 881,575, Gulk, Mar. 10, 1908; 1,805,142, Hippenmyer, May 12, 1931; and 911,320, Muller, Feb. 2, 1909.

Improved Method of Washing Glassware, Fig. 5. Patent No. 2,419,805. This patent does not relate to the manufacture of glass, but if this method is as successful as appears from the patent, manufacturers of re-used glass containers, such as milk bottles, may be relieved from a lot of headaches. The patent inhibits the dissolution of alkali from glass during washing operations. It is an invention of Walter F. Wegst and Leslie R. Bacon, who assigned it to Wyandotte Chemicals Corporation.

It is usual to use washing solutions having a high alkaline strength; in fact, some states require a minimum NaOH content in bottle washing. A caustic alkali, such as sodium hydroxide, is most commonly used. It is well known that such washing compounds dissolve some of the surface of the glass when used in commercial washing machines. The injurious results of this are well known in the glass business.

These inventors have discovered that compounds of beryllium added to the alkali washing solution in the amount of from 0.05 per cent to 2.5 per cent BeO content practically eliminate the dissolving action on the glass. This may be added in the form of beryllium sulfate ($BeSO_4 \cdot 4H_2O$).

A comparison between the method of this invention and the old method was shown in weight loss of the bottle and in one test was as follows:

	Weight Loss	
Solution Strength	0.3% BeO Content Beryl-NaOH Fusion Product	NaOH Alone
	Grams	*Grams*
1%	0.016	....
	0.013	....
	0.010	....
	0.010	....
Average	0.0122	.853
3%	0.024	....
	0.014	....
	0.012	....
	0.009	....
Average	0.0147	1.470
5%	0.031	....
	0.039	....
	0.015	....
	0.021	....
Average	0.0265	1.748

Fig. 5 is a curve showing a similar comparison of the old and new washing methods and also showing that the new invention has some advantages over pure water.

The following references are of record in the file of this patent: United States Patents 2,238,206, Adamoli, Apr. 15, 1941; 2,284,743, Kawecki et al., June 2, 1942; and 2,241,984, Cooper, May 13, 1941. Foreign Patent 435,092, British, Sept. 13, 1935. Other References: Production of Beryllium Oxide from Beryl, Winter, dissertation pub. in N. Y., 1939, pages 18-19. Production of Beryllium Oxide from Beryl, Winter, page 24.

QUALITY CONTROL SOCIETY CONVENTION

The first annual convention of the American Society for Quality Control is being held June 5 and 6 at the Hotel Sherman in Chicago.

Outstanding speakers from all over the country will, in thirty-five clinical sessions, present stories of the application of quality control principles to fields ranging from inventory control to ammunition. In addition, about thirty exhibitors will demonstrate the value of their equipment as aids to the quality control operator.

SOME COMMENTS ON THE ATLANTIC CITY CONVENTION

Editor,
THE GLASS INDUSTRY

The attendance at the Ceramic Society's annual meeting was large. The registration of members is reported to have reached 1,650. Members were housed in a number of hotels; meetings were held in Convention Hall. Atlantic City is laid out for this arrangement. It is probably a good arrangement for the city, but is not so convenient for the delegates. A number of them expressed themselves as disliking it: one or two, on the other hand, reported that they enjoyed the walk.

The Edward Orton Memorial Lecture by Dr. Gibson seems to have met with very general approval, and may deserve more detailed consideration when available in printed form.

The Glass Division meetings, which in the past have usually begun Tuesday morning and finished Wednesday evening, this time began Tuesday afternoon and were slated to continue till the end of Thursday afternoon. This is a perfect scheme for ruining a whole business week, and goes in exactly the opposite direction to that recommended by the present writer at the Columbus meeting of the Glass Division last fall, of trying to get the sessions so that they either occupy the weekend, or permit use of a weekend for traveling to or from the meeting. As it was, many delegates left Wednesday evening or Thursday morning.

The number of technical papers was considerable, more than necessary. Their average quality was perhaps higher than usual, and some novel ideas were propounded. Discussion in general was livelier than at most such meetings. Attendance reached the four-hundred level, or thereabouts, at times, and was generally 200-300. This is a convention in itself, and it would probably have functioned more smoothly if it *had* been a convention by itself.

Some of the papers were well delivered. A woman speaker, and one or two of the men, came in for general very favorable comment on this score. There was not much actual *reading* of papers, and this was a big improvement over some recent gatherings. A few speakers *read* parts of their papers. This proceeding is to be condemned. The speaker ought to know what is in his paper, and be able to tell it, without looking up anything except perhaps numerical values.

A number of speakers are still under the impression that tabular matter is suitable for projection by lantern slide. This is very rarely the case, and most such slides were illegible from the rear rows of seats. Many diagrams were illegible also, and some were not legible half way from the rear. The fact that a diagram, graph, or chart is carefully prepared and will reproduce well in the printed version, is no evidence that it will be suitable for the lecture room. Diagrams, like the talk itself, should be essentially different from the printed version; they should be simplified, stressing only essentials, adapted for quick grasping, not for meticulous detail.

Some speakers took much more time than they asked for, and much more than was necessary. Scientific papers, like sermons, can get too long. The best way to ruin a good sermon, or a good paper, is to drag it out.

One or two speakers not only took a great deal of time, but they took it for a long dissertation on chemistry principles. There is perhaps a place for such papers in the Division's activities, perhaps as part of the printed record. But a number of delegates complained at having to listen for an hour to teen-age stuff. The members of the Glass Division would probably make no claim to intellectual eminence, but their intelligence should not be grossly underrated.

One of the most obvious features of the proceedings was the incessant coming and going of delegates into and out of the Glass Division meeting room. This went on throughout the "papers", not merely at the end of a paper. They came in, not to hear the paper, but to see if someone else was there. They went out when satisfied that he wasn't. This is likely to occur when the members are housed in different hotels, and do not have an entirely convenient rendezvous. A good deal of talk was going on in the room itself during most of the papers, and every time the door was opened, the noise of a great many more impromptu conferences raised the decibel level. The speakers managed very well in spite of the distractions, but the distractions were numerous, and the quality of the meeting suffered from them.

The meetings can be improved by more attention to detail, as set forth above, but in the writer's opinion the annual gathering of the American Ceramic Society has now reached unwieldy proportions and will provide an increasingly unsatisfactory opportunity for technical sessions. These should be concentrated more and more in separate convenings of the Glass Division.

F. W. Preston

DYEING PROCESS FOR FIBERGLAS YARN

Development of a new process of filament coating whereby a thin protein film (gelatin type) is applied to Fiberglas yarns as they are formed has made it possible to dye the yarns with ordinary dyes and by commonly used methods.

The protein film that is applied to the filaments while the yarn is being formed represents only one to two per cent, by weight, of the finished yarn but with this small amount of film, improved depth of color has been achieved due to absorption of the dyes by the film on the large surface area presented by the multiple-filament yarn.

Soluble vat dyes are the most resistant to fading and washing and direct dyes, acid dyes and chromes give the deepest shades. Resin after-treatment is used to reduce crocking when necessary. Dyeing takes place rapidly chiefly because of the large surface area and because the dyes do not penetrate the fibers. The yarns do not shrink or swell during the dyeing process. When used in woven fabrics in combination with other yarns, the Fiberglas yarns help prevent stretching during the finishing processes. Dyed Fiberglas yarns for decorative uses have a minimum of 80 hours sun-fastness.

FEDERAL GLASS NAMES PURCHASING AGENT

Federal Glass Company has recently announced the appointment of Lyle Treadway to the post of Purchasing Agent to succeed Morris G. Woodhull, who recently retired after 37 years of service with the company.

Mr. Treadway has been associated with Federal Glass Company for ten years during which time he has served in various capacities and departments.

Research Digest

Spectrochemical Analysis of Ceramics and Other Non-Metallic Materials

The spectrograph is not generally thought of as being a suitable tool for the quantitative determination of the major constituents in ceramic materials. E. K. Jaycox (*Journal of the Optical Society of America*, March 1947) however, describes a procedure which is applicable to the quantitative spectrochemical analysis of ceramics, ashes, slags, and other such materials for the determination of most of the common metals and their oxides. These include aluminum, boron, barium, beryllium, calcium, copper, chromium, iron, lithium, magnesium, manganese, sodium, lead, silicon, titanium, zinc and zirconium in the general range of 0.30 to 70.0 per cent.

The drawback in spectrographic determinations of major constituents has been that the densities of their principal lines are usually too high for accurate measurement by densitometry. In addition, at high concentration, self-absorption becomes an important factor. The reduction of the concentration of the element in question by the addition of a buffer material eliminates most of the troubles arising due to self-absorption and, at the same time, reduces the densities to measurable ranges.

TABLE I

Sample	% Compound	% Spectro	Chemical	Δ	%Δ
F-66	Al_2O_3	7.61	7.58	+0.03	+0.4
S-7	Al_2O_3	1.04	1.0	+0.04	+4.0
Sierramic Talc	Al_2O_3	1.07	1.15	—0.08	—7.4
N.B.S. No. 76	Al_2O_3	36.2	37.7[1]	—1.5	—4.0
F-66	BaO	16.4	15.74	+0.76	+4.8
S-7	BaO	4.13	4.17	—0.04	—1.0
F-66	CaO	0.94	0.54	+0.30	+47.0*
S-7	CaO	0.64	none	—	—*
Sierramic Talc	CaO	0.42	0.43	—0.01	—2.3
N.B.S. 76	CaO	0.265	0.27[1]	—0.005	—1.8
F-66	Fe_2O_3	1.15	0.91	+0.24	+26.0*
S-7	Fe_2O_3	0.71	0.66	+0.05	+7.5
Sierramic Talc	Fe_2O_3	1.37	1.39	—0.02	—1.4
N.B.S. No. 76	Fe_2O_3	2.30	2.37[1]	—0.07	—3.0
F-66	MgO	23.7	24.6	—0.9	—3.7
S-7	MgO	50.2	50.9	—0.7	—1.4
Sierramic Talc	MgO	31.6	31.2	+0.4	+1.3
F-66	SiO_2	47.1	50.12	—3.02	—6.0
S-7	SiO_2	44.5	42.99	+1.51	+3.5
Sierramic Talc	SiO_2	57.2	58.8	—1.6	—2.7
N.B.S. No. 76	SiO_2	56.0	54.7[1]	+1.3	+2.4
Ash-Tar	ZnO	0.53	0.55	—0.02	—3.6
				Av. %Δ	±3.3

*Values omitted from average.
[1]N.B.S. certified values.

TABLE II

	1	2	3	4	5	6
BaO	8.3%	5.6%	6.8%	4.0%	6.7%	—
CaO	0.6	0.6	0.6	<0.2	<0.2	—
MgO	31.0	25.0	29.4	24.8	25.4	—
Al_2O_3	3.3	3.8	5.6	4.1	8.0	29.6
Fe_2O_3	1.1	1.4	1.6	1.3	1.7	0.34
SiO_2	54.6	59.0	56.1	64.0	51.0	65.7
TiO_2	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Total	99.9%	96.2%	101.1%	96.5%	94.0%	96.6%

	7	8	9	10	11	12
BaO	<1.0%	<1.0%	<1.0%	—	7.6%	5.8%
CaO	1.0	1.0	<1.0	0.2%	0.4	0.3
MgO	25.9	29.6	<1.0	1.0	30.0	29.0
Al_2O_3	7.4	3.2	1.3	1.7	3.8	3.2
Fe_2O_3	1.6	1.0	<1.0	0.13	1.7	1.5
SiO_2	54.0	64.4	16.8	4.0	51.0	53.0
TiO_2	<1.0	<1.0	75.0	80.0	5.3	5.0
Total	91.9%	101.2%	97.1%	87.0%	99.8%	97.8%

This buffering principle is one employed when dealing with ceramic materials.

A representative sample is ground to a fine powder and mixed with a suitable buffer material. Lead monoxide, bismuth trioxide, cupric oxide, nickel oxide and barium nitrate have been used successfully as a buffer and internal control. Of these, the black cupric oxide (CuO) has been found to be very satisfactory for ceramic materials. The basic mixture employed is one part of sample to 19 parts of pure cupric oxide, to which is added for additional buffering, 40 parts of pure carbon dust. Such a mixture is satisfactory for the determination of most elements in the range of 0.30 to 35.0 per cent. When it is desired to determine an element in any amount greater than 35 per cent, it is better to use a mixture in the ratio 1:39:80. A ratio of 1:9:20 is sometimes used when the concentration of the element sought is less than one per cent. Standards are always made up in the ratio 1:19:40 and a factor used in the final calculations when samples have been prepared in a different ratio.

Spectra are obtained of the samples and of an appropriate series of standards. Determinations of the amount of element sought are made in most cases by the well known internal standard technique; in others by the simple comparison standard procedure.

The data in Table I indicate the accuracy to be expected of this procedure. Nineteen out of twenty-two comparisons with chemical determinations are in good agreement. Three are not. These have been omitted from the average. From this work and other work not reported, the precision is, in general, better than ±100 parts/thousand.

In Table II is shown the complete spectrochemical quantitative analysis of twelve ceramic samples whose composition was unknown. Qualitative analyses were first run, followed by quantitative analyses for all elements estimated to be greater than 0.5 per cent. The total sum of the amounts of compounds found should add up in each case to 100 per cent ± the precision of

(*Continued on page* 318)

KIMBLE GLASS APPOINTMENTS

The appointments of Stanley J. McGiveran as General Sales Manager and Maxson A. Eddy to be in charge of manufacturing were recently made known by Kimble Glass Division of the Owens-Illinois Glass Company. Both Mr. McGiveran and Mr. Eddy were elected Vice Presidents of Owens-Illinois at the last meeting of the Board of Directors.

Mr. McGiveran joined Owens-Illinois in 1927 upon

Maxson A. Eddy Stanley J. McGiveran

graduation from the University of Wisconsin. In 1936 he became advertising and merchandising director and in 1938 was named General Manager of the Insulux Products Division. In 1941 he became Vice President and General Sales Manager of the Owens-Illinois Can Company, serving in that capacity until sale of the Can Company in 1944.

Mr. Eddy is a graduate of the University of Connecticut. He joined Owens-Illinois in 1931 and served as Manager of the Streator plant and then the Terre Haute plant. He joined Kimble Glass Company in 1938 and was elected Vice-President and General Manager of the company in 1939, serving in that capacity until the company became a Division of Owens-Illinois in February.

The Kimble Division plans to operate all the present Westwood facilities now occupied by the Closure Division of Owens-Illinois in Toledo when that division moves to its new and larger plant in St. Charles, Illinois. Installation of new furnaces and Kimble equipment will be made as rapidly as Closure machinery is moved to St. Charles. The Kimble operation on Westwood Avenue will be immediately adjacent to a furnace and laboratory now under construction for general glass research.

L-O-F EXPANDS SAFETY GLASS PLANT

With an eye to the larger production and continued heavy demand for plate and window glass for building construction, Libbey-Owens-Ford Glass Company has announced that it would begin building an extension to its safety glass plant in Ottawa, Illinois.

The structure, 416 feet long and 122 feet wide, will have walls of fluted, insulated aluminum with half of the area in glass to provide maximum daylight. It will have a flat roof designed to aid in cooling.

Larger assembly facilities, new washing machines and enlargement of air-conditioning equipment for the glass laminating operations will result from the additional space.

Construction will be supervised by the A. Bentley & Sons Company, Toledo, Ohio. Plans were prepared by the company's Engineering Division and it is expected that the extension will be completed in December.

DU PONT MAKES APPOINTMENT

The appointment of Edgar A. Thronson as Assistant Director of the Technical Division of the Electrochemicals Department was recently announced by E. I. du Pont de Nemours & Company.

Mr. Thronson has been with Du Pont since 1929 and has most recently been a special assistant to D. O. Notman, Director of the Technical Division.

He started work as a development chemist at the Niagara Falls plant soon after he was graduated from the University of Wisconsin and became a process supervisor in 1934. In 1937 he became an area manager was later in charge of all process improvement activities at Niagara Falls.

BALL BROTHERS APPOINTMENTS

Edmund F. Ball, Executive Vice President of Ball Brothers Company, has announced four changes in managerial assignments. John W. Fisher, formerly Manager of all Ball glass factories, has been appointed General Manager of Container Manufacturing. In his new post, Mr. Fisher will supervise all processing operations both at the Ball glass plants and at the Ball paper mills in Muncie and Noblesville, Indiana.

John C. Schwab has been advanced to Glass Factories Manager to succeed Mr. Fisher. He will be responsible directly for operations at all Ball glass container plants, including those of the Muncie Works.

Advanced to the post of General Superintendent of the Muncie plant under Mr. Schwab is Fred Kirk. The fourth change was the appointment of D. K. Addie as Technical Adviser to the Glass Division.

It has also been announced that Donn Sutton has been retained as Public Relations Counselor for the company. Mr. Sutton, who was formerly Editor-in-Chief of NEA Service, will be located in Chicago.

APPOINTMENTS AT FERRO ENAMEL

At the annual meeting of the Ferro Enamel Corporation, all old directors were re-elected and Messrs. W. B. Lawson, C. D. Clawson, F. S. Markert and G. W. Wallace were added to the Board of Directors. R. A. Weaver was elected Chairman of the Board and will continue to be the chief executive officer of the company. J. D. Henry was elected Vice-Chairman of the Board.

C. D. Clawson, who has been Vice President in Charge of Sales, Research and Service, was elected President, and F. S. Markert, who has been Vice President in Charge of Manufacturing and Engineering, was elected Executive Vice President and General Manager. Dr. G. H. McIntyre, who has been Director of Research, was elected Vice President of the company.

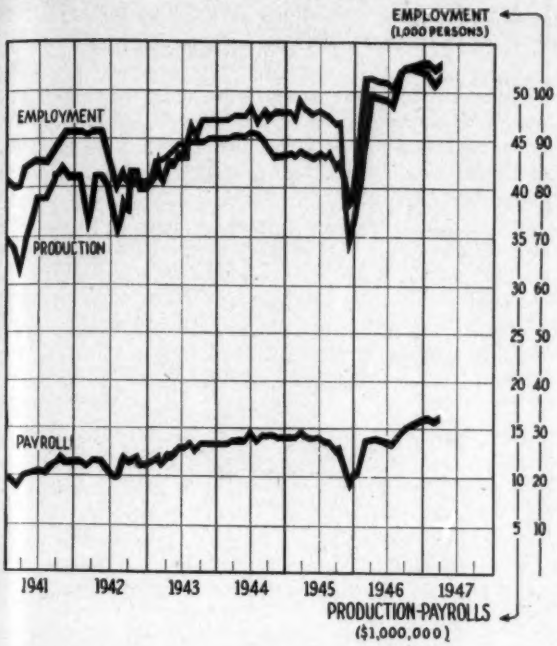
PITTSBURGH PLATE QUARTERLY REPORT

Unhampered by strikes in the Glass Division which affected the first quarter of 1946, Pittsburgh Plate Glass Company's sales for the first quarter of 1947 amounted to $62,589,324 as compared with $37,177,894 for the same period last year.

Net income for the first quarter of 1947, after all deductions including Federal and State taxes on income, amounted to $6,729,214, equivalent to 76 cents per share of the company's outstanding stock. Comparable net income for the same period of 1946 was $3,330,825, equivalent to 37 cents per share.

CURRENT STATISTICAL POSITION OF GLASS

THE GLASS INDUSTRY'S INDEX



March 1947 activity in the glass industry, according to the Production Index, rose close to 5 per cent to reach an estimated total of $57,000,000. The production figure reported for the previous month was $54,500,000. For March 1946, production was an estimated total of $49,500,000, which is about 15 per cent below March this year. Total output for the first quarter of 1947 is an approximate $168,500,000 as compared with $136,000,000 during the corresponding period in 1946.

Employment and payrolls: During the month of March 1947, employment rose about 2 per cent to a total of 104,000 persons. The number of persons employed during February was 101,500. During March 1946, employment in the glass industry was 102,000, which is close to 2 per cent under the March 1946 figure.

Payrolls for March 1947 also rose to an approximated $16,000,000. This figure is close to 5 per cent above the figure reported for the preceding month which was $15,500,000. During March 1946, payrolls were an estimated $13,500,000, or about 18 per cent less than for March this year. Glass manufacturers have paid out an estimated $47,500,000 during the first quarter of 1947 as compared with $37,100,500 during the same period in 1946.

Glass container production, based on figures released by the Bureau of Census, fell off slightly for the month of April 1947 to a figure of 10,317,201 gross. This is about 3 per cent below the 10,640,482 gross reported for March 1947. Production during the month of April 1946 was 9,529,645 gross, which is about 8 per cent under the figure for April this year. Total production thus far in 1947 has reached a total of 41,381,821 gross. During the corresponding period in 1946, the total production was 38,233,137 gross.

April 1947 shipments also fell off slightly from the 10,012,450 gross reported for the previous month. April's shipment figure is 9,982,640 gross, only a fraction of 1 per cent below March. Shipments for April 1946 were 9,660,542 gross, which is about 3 per cent below April 1947. Total shipments made during the first four months of 1947 are 39,505,889 gross as compared with 38,299,673 gross shipped during the same period in 1946.

Inventories of glass containers on hand at the close of April 1947 were 5,442,586 gross. Previous figures were 5,140,116 gross at the close of March 1947 and 4,167,899 gross at the close of April 1946.

(*Continued next page*)

GLASS CONTAINER PRODUCTION AND INVENTORY

(All figures in gross)

		Production April 1947	*Stocks April 1947*
Foods; Medicinal & Health Supplies; Chemicals, Household, Industrials; Toiletries & Cosmetics	Narrow Neck	3,212,128	2,195,788
	Wide Mouth	3,016,519	1,418,493
Dairy Products		372,097	212,494
Home Canning		201,522*	672,671
Beverages, Returnable		936,631	451,171
Beverages, Non-returnable		.....	.....
Beer, Returnable		1,308,848	135,086
Beer, Non-returnable		134,376	12,121
Liquors		856,607	199,141
Wines		145,546	102,919
Packers' Tumblers		132,927	42,702
Total		10,317,201	5,442,586

*This figure represents Fruit Jars only.

GLASS CONTAINER SHIPMENTS

(All figures in gross)

	April 1947
Narrow Neck Containers	
Foods	1,048,154
Medicinal & Health Supplies	1,099,714
Chemical, Household, Industrials	503,495
Beverages, Returnable	853,636
Beverages, Non-returnable	.....
Beer, Returnable	1,273,082
Beer, Non-returnable	69,054
Liquors	860,156
Wines	132,407
Toiletries & Cosmetics	392,853
Sub-Total (Narrow)	6,232,551
Wide Mouth Containers	
Foods	2,178,600
Dairy Products	354,408
Home Canning	161,188
Medicinal & Health Supplies	312,617
Chemical, Household, Industrials	115,291
Toiletries & Cosmetics	143,027
Packers' Tumblers	128,049
Sub-Total (Wide)	3,393,180
Total Domestic	9,625,731
Export Shipments	356,909
Total Shipments	9,982,640

Attention . . .

Glass Tank Operators

For Maximum Life SPECIFY

C · S · R

CAST SUPER REFRACTORY

For

Mantels, Feeder Parts, Tuckstones, Burner Blocks, Port Covers, Port Bottoms, Port Arches, Port Skews, Port Baffles, Lintels, Jambs, Bridgewall Covers, etc.

C.S.R. ***has excellent resistance to***

HIGH TEMPERATURES
CORROSION
SHRINKAGE
SPALLING

C.S.R. ***is***

VACUUM CAST
ACCURATE TO SIZE
UNIFORM TEXTURE
ECONOMICAL

●

Write for Full Particulars

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High Grade Refractories for Over 50 Years

4070 NORTH FIRST STREET ST. LOUIS 7, MISSOURI

Plate glass production for the month of April 1947 dropped off to 21,419,088 sq. ft. The previous month's production was 22,605,264 sq. ft. This represents a decrease of about 5 per cent. During April 1946, plate glass production was 18,514,580 sq. ft., or 15 per cent below April this year. Total production thus far in 1947 is 86,271,503 sq. ft. as compared with 56,011,614 sq. ft. produced during the January-April period in 1946.

Automatic tumbler production for the month of April 1947 increased close to 6 per cent to a total of 6,639,261 dozens. The March figure was 6,272,261 dozens. Production during April 1946 was 6,935,081 dozens. Shipments during April also indicated an increase and were reported at 6,140,403 dozens. This is about 2 per cent over shipments for March, which were 5,974,554 dozens. For April 1946 shipments were 7,415,951 dozens. Stocks on hand at the close of April 1947 were 6,262,482, or 12 per cent greater than at the close of March. The March figure was 5,575,294 dozens. Stocks at the close of April 1946 were 4,410,267 dozens.

Table, kitchen and household glassware: Manufacturers sales of machine-made table, kitchen and household glassware for the month of April 1947 were 3,453,687 dozens. This is about 7 per cent over the March figure, which was 3,213,252 dozens. Sales during April 1946 were 4,100,213 dozens. Total sales for the 12-month period ending April 1947 were 44,429,834 dozens.

COMMERCE DEPARTMENT REPORTS ON ARTIFICIAL OPTICAL FLUORITE

According to a report issued by the Office of Technical Services, Department of Commerce, great success was achieved during the war in growing artificial optical fluorite crystals many times as large as those found in natural fluorspar and superior to natural crystals for making optical glasses. Crystals which were grown to six inches in diameter were found to have excellent optical homogeneity, the report states.

The 187-page report was written by Dr. Donald C. Stockbarger and Miss Marie Early of Massachusetts Institute of Technology for the Office of Scientific Research and Development.

The M.I.T. researchers grew approximately 1,500 crystals, many of which were made available to governmental and other laboratories for experimental use and tests. Dr. Irvine C. Gardner, Chief of the National Bureau of Standards optical instruments section, in commenting on the report, stated that lenses made of artificial fluorite showed an index of refraction very close to that of natural fluorspar. However, the small size of natural crystals—usually ½ to ¾ of an inch—has limited their use to lenses of small diameter. The larger crystals grown by the M.I.T. process are an important addition to the materials available for making special-property optical lenses, Dr. Gardner added.

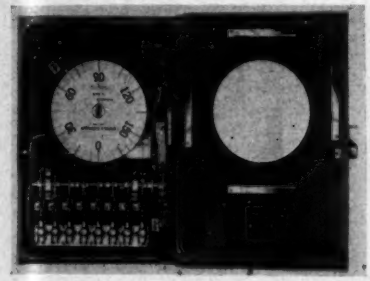
The report, PB-33253, "Artificial Optical Fluorite", is available through the Office of Technical Services, Department of Commerce, Washington 25, D. C. Microfilm is $4.00 and photostat, $13.00.

NEW EQUIPMENT AND SUPPLIES

TIME CYCLE CONTROLLER DEVELOPED

The Bristol Company, Waterbury, Conn., has developed a new multiple-cam time cycle controller for timing mechanical operations in industrial processes. Known as Model C500 Impulse-Sequence Cycle Controller, it is designed for use on plant processes where a number of factors must be accurately timed according to a fixed program.

Time measurement and pilot valve



operation are handled by separate mechanisms. Separation of these two basic functions made possible a design that gives accurate timing of the factors under control, high speed and torque for pilot valve operation and flexibility of application.

Timing is accomplished by a Telechron-driven aluminum disc on which is printed a 25-inch time scale. The desired schedule of operations is incorporated into the controller by cutting notches with a notching punch on the time scale. The locating of these notches determines the time of operation of the cam mechanism. Discs for new cycles or schedules of operation can be made.

All controllers are drilled for eight cams and pilot valves. Additional cams and pilot valves up to a total of eight can be easily added by the user to controllers originally made up with less than eight cams.

DIAMOND ABRASIVE CORE DRILL

Felker Manufacturing Company, Torrance, California, has announced the development of the Felker Di-Met Core Drill which is designed to drill holes any depth in all hard, brittle, nonmetallic materials. Increased drilling speed is due to the method of supplying coolant through the drill stem to the special metal-bonded diamond abrasive rim. Due to coolant pressure, chips and sludge are flushed from the kerf as fast as developed and since coolant supply is constant, the drill functions without heat, regardless of hole depth.

The Core Drill may be used in drill presses, on portable electric drills or directly coupled to motor shafts. It operates in any position and usually requires only a few seconds per inch of travel when drilling most materials.

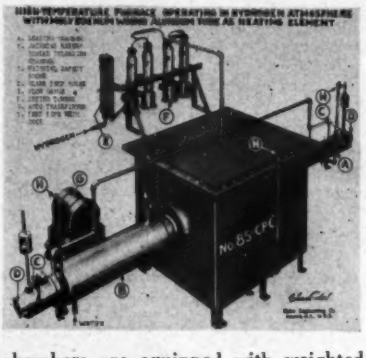
Applications are numerous in drilling or coring glass, tile, porcelain, ceramics, gem stones, granite, etc.

EISLER HYDROGEN ELECTRIC FURNACE

Eisler Engineering Company, Newark 3, New Jersey, is manufacturing a Hydrogen Electric Furnace to degasify the metallic material before being used in the manufacture of incandescent lamps, radio and electronic tubes and to deprive it radically from all contaminating substances, especially oxides and moisture.

The inside of the steel-fabricated, hermetically sealed furnace is fully fire-brick insulated and the heating element operating in an atmosphere of constant flow of hydrogen consists of a molybdenum wond alundum tube capable of withstanding temperatures as high as 3000° F.

The furnace is supplied with a tubular loading chamber and, on the opposite side of it, with a jacketed water cooling unloading chamber. Both



chambers are equipped with weighted safety-doors and glass peep holes on its end. It is supplied with the necessary piping and with a proper auto transformer for heat regulation, either standard type with eleven point tap switch or special type with about eighty steps.

NEW TYPE HIGH-VACUUM FURNACE

Eitel-McCullough, Inc., 1570 San Mateo Avenue, San Bruno, California, has developed a new type of high vacuum furnace which is capable of continuous operation at temperatures in the 1800C. region. The standard type consists of three chambers integrated into a single enclosed cubicle. Cycling circuits are incorporated so one chamber can be in the treatment phase while one is under preliminary pumping and the third is being reloaded.

Heating of the furnace is accomplished by large-diameter tungsten elements which involve low voltage. This minimizes ionization problems. Each chamber of the furnace is equipped with a special high-speed oil diffusion pump capable of maintaining high vacuum during the most difficult outgassing operations.

BRYANT BLOWER LINE

Bryant Heater Company, Industrial Division, 1020 London Road, Cleveland, Ohio, has announced a new line of light-weight "Hi-Flo" blowers designed for constant pressure output over a broad capacity range.

The new direct-connected centrifugal machines are constructed of aluminum housings, bases and side plates with a simplified light-weight steel impeller for smooth operation and low bearing load.

Any one of seven outlet positions may be chosen in a simple change-over scheme requiring only a wrench for adjustment. A flanged outlet connection does away with the need for pipe unions in the air line. A specially designed hub arrangement has been incorporated in the blowers to permit the use of standard 3450 rpm. motors with regular shaft extension.

CATALOGUES RECEIVED

Frazier-Simplex, Inc., 436 East Beau Street, Washington, Pa., has recently released a catalogue on Batch Feeding Systems for glass plants.

The catalogue describes the Blanket Batch Feeding System and the Screw Type Feeding System, with illustrations and descriptions of the suspended shadow wall and complete batch plants for glass factories. It is illustrated with photographs and engineers' drawings showing the operation of the system.

Brown Instrument Company, Division of Minneapolis-Honeywell Regulator Company, Philadelphia 44, Pa., has issued a Data Sheet, No. 1.4-1, devoted to the Brown Temperature Control System for Glass Feeders.

Included with illustrations and a diagram of a glass feeder control system is information on Components of System, Equipment Specifications for Two-Zone Feeder, Optional Equipment, Operation of Control System, Operation of Signal Lights, Rear Channel Temperature Control or Indications for Manual Regulation and Result of Extensive Commercial Installations.

Lustra Corporation of America, 40 West 25th Street, New York 10, New York, has issued a folder on fluorescent lamps, "A Miracle of Light," describing the four classes of Daylight, 3500° White, Soft-White and 4500° White Lustra fluorescent tubes. Newest of the four is the 4500° White Lustra tube combining the blue-white of daylight with white light.

Each type of fluorescent light is described and the best applications given for each. Fluorescent lighting and its advantages is discussed.

THE GLASS DIVISION AT ATLANTIC CITY . . .

(*Continued from page* 298)

erable temperature range, using fused samples between platinum electrodes and a conventional Wheatstone bridge circuit on 1) sodium chloride and potassium chloride, 2) a commercial hydrated sodium silicate and a 30 per cent Na_2O-70 per cent SiO_2 glass, 3) soda-lime-silica glasses containing iron or nickel oxides and 4) a commercial crown glass.

Measurements were made during both heating and cooling cycles. Although the two curves sometimes had somewhat different appearances, the actual transition temperatures were so nearly the same that no effort was made to differentiate between them in the interpretation.

In plots of log resistance versus 1/T, straight lines whose slopes changed at definite temperatures were drawn through the data. The temperatures at which such discontinuities occurred were classified into Ritz type series which can be expressed by equation (1).

$$T_x = ct\ (1/n_o^2 - 1/n^2) \qquad (1)$$

T_x = transition temp. in ° K.

ct = series constant in ° K.

n_0 = base number of series.

N = term number of series and takes successive values $(n_o + 1)\ (n_o + 2), \cdots \infty$.

T^∞ = series convergence in ° K = value of T_x for $(n = \infty)$.

The constants, ct, no and T^∞ of the Ritz type series have been found for the elements oxygen, sodium, magnesium, silicon, chlorine, potassium, calcium, iron and nickel and are listed in Table I.

An analysis of this work indicated that these measurements have given the same series constants for all atoms common to the different specimens used. A relationship is indicated between the number of series characteristic of a given chemical element and its position in the periodic table. As a general rule, values of the series constant, ct, appear to increase with increasing base constant, n_o, up to a value of n_o which depends on the element in question after which the series constant remains the same.

This thermal series transition explanation was also shown to account for the discontinuities reported about fifteeen years ago by W. E. S. Turner and his coworkers in studies of thermal expansion and electrical resistance of glasses vs. temperature.

Oxidation and Reduction of Glasses by Means of Electrolysis. *By G. E. Rindone, Evelyn C. Marboe and W. A. Weyl, Glass Science, Incorporated, State College, Pa.*

In many glass making processes, such as fining, decolorization and the development of colors, the oxidation and reduction reactions that take place in the melt are the predominate factors in the success of the process. In ordinary chemical reactions at or around room temperature, such reactions are not too difficult to perform due to the many materials that are available for these reactions at glass making temperature. However, such oxidation and reduction reactions become difficult due to the fact that such agents decompose or otherwise become inactive at glass manufacturing temperatures. Oxidizing or reducing agents that will do a job at such temperatures are strictly limited.

This need for controlling the state of oxidation or reduction of glass led to this present investigation on the possibilities of oxidizing or reducing a melt of glass by the means of electrolysis. The addition or withdrawal of electrons is the most direct way to reduce or to oxidize an ion.

If a direct current is allowed to pass through an electrolyte, oxidation processes are observed around the anode because of the removal of electrons from the electrolyte. At the cathode, reduction takes place. If an electric current is passed through a soda-lime-silica glass containing the ions Si^{4+}, Ca^{2+}, Na^+ and O^{2-} as the main constituents, only one of the ions, namely O^{2-}, can become a source of electrons. At the anode, therefore, oxygen ions are discharged and gaseous oxygen is liberated from the melt. Such a method would allow oxidation or reduction procedures to be carried out in the melt without recourse to chemical materials such as are normally used. An apparatus was therefore devised for the electrolytic oxidation and reduction of molten glass in which a refractory diaphragm was used to separate the anodic and cathodic reaction zones.

Low melting alkali-borate and alkali phosphate glasses containing a minor addition of colorant were electrolyzed by this procedure using voltages up to 10 volts. Among the various colorants that were successfully reduced or both reduced and oxidized by this method were sulphite, selenites, titania, copper, iron, chromium, manganese, ceria and vanadium. This electrolysis procedure was also used to lower the "gas content" of glasses and to increase infra-red transmission by the removal of water from the glass.

Pyrometry for the Glass Industry and Introduction to Principles of Automatic Control. *By V. L. Parsegian, Tagliabue Division, Portable Products Company, Brooklyn, N. Y.*

Since the viscosity of glass varies very rapidly with change of temperature and the proper working of glass and the annealing of the finished product are largely determined by viscosity conditions, the proper measurement and control of temperature are of paramount importance to the glass industry.

The author discussed how temperatures are measured, the International-Temperature Scale, indicating and recording thermometers, electrical methods, the thermocouple circuit, thermocouple materials, thermoelectric tables, the testing of thermocouples, thermocouple stability, the reference junction, instruments for thermoelectric thermometry including the millivoltmeter type and the potentiometer type, resistance thermometry, optical and radiation pyrometry, photoronic cell pyrometry and the general principles of automatic temperature control.

The original paper is much too long to be successfully condensed. Its appearance in published form will prove to be a good guide and reference for those interested in temperature measurement in the glass industry.

Voltage Anomalies of the Glass Electrode and the Chemical Durability of the Glass. *By Donald Hubbard and G. F. Rynders, National Bureau of Standards, Washington* 25, *D.C.*

The ability of a glass to function satisfactorily as an indicator of the hydrogen ion activity of aqueous solutions appears to be largely determined by two properties of the glass, namely, the hygroscopicity (water sorption) and the uniformity of the chemical durability over an extended pH range. Glasses of inadequate hygroscopicity produce electrodes of high resistance whose pH responses fall appreciably below the theoretical dictates of the Nernst equation:

$$\Delta E = 0.000198T\ \Delta\ pH$$

On the other hand, solutions that cause detectable changes in the durability of the glass also bring about departures (errors) from the same straight line relationship.

The glass whose hygroscopicity and durability characteristics have most nearly fulfilled the requirements for pH measurements is one of composition SiO_2-72%, Na_2O-22%, and CaO-6% (Corning 015). Although this glass combines the two necessary properties of adequate hygroscopicity and uniform durability to a considerable degree of success, electrodes prepared from it exhibit voltage departures in the "super acid" range and even more conspicuous errors in alkaline solutions above pH 9.

A series of electrodes of this glass were prepared to ascertain if voltage departures always occurred in regions of change in the chemical durability of the glass and to determine the extent to which this takes place. These electrodes were simple metal-filled bulbs and were used in combination with a hydrogen electrode, while the attack data were made by means of an interferometer method.

Results confirmed and extended the earlier findings that in every case voltage departures of the electrode are ac-

(*Continued on page* 314)

Unretouched photo—ports are blocked with canvas to exclude drafts during examination.

EXCELLENT OPERATION PLUS GOOD REFRACTORIES...

OPERATING DATA	
Melting Area, Not Including Doghouse (Sq. Ft.)	518.5
Tank Depth, Metal Line (Inches)	34
Total Days Life	1150.0
Total Operating Days	1089.8
Total Idle Days	60.2
Tons Glass Delivered	114,103.1
Tons Glass Per Operating Day	104.7
Sq. Ft. Melting Area Per Ton Glass Per Day	4.95
Tons Per Square Foot Per Life	220.0

THE furnace shown above has just finished a campaign of 1089.8 operating days, producing 220.0 tons of amber bottle glass per square foot of melting area during the campaign! (Rate of pull — 4.95 sq. ft. per ton per day.)

Superior glass-production records are primarily the result of superior operational techniques. This example is no exception. But it goes without saying that the operators are pleased with the performance of the Corhart Standard Electrocast with which the furnace was built — and we of Corhart* are pleased that these operators have been consistent users of Corhart Electrocast Refractories for many years.

Corhart Refractories Company, *Incorporated*
16th and Lee Streets, Louisville 10, Kentucky
In Europe: L'Electro Refractaire, Paris.

*Not a product, but a trade mark.

QUALITY ECONOMY ENDURANCE

CORHART ELECTROCAST REFRACTORIES

THE GLASS DIVISION AT ATLANTIC CITY . . .

(*Continued from page* 312)

companied by durability changes in the glass. The pronounced voltage departures in the alkaline region and in hydrofluoric acid solutions are accompanied by conspicuous attacks on the glass. Dilute solutions of acids that do not form soluble compounds of silica cause swelling of the glass. This swelling is repressed as the concentration of the solution is increased. As is to be expected from the distribution law and Donnan Membrane considerations, this repression of swelling was also brought about by high concentration of organic acids and salts as well as by the so-called "strong" acids. The attack of Corning 015 glass by alkaline solutions of different ions was found to be in the order of $Na^{+} > Li^{+} > K^{+} > Ba^{++} > NH^{+}_{4}$, which is the same order as dictated for these ions by voltage departure data.

A Study of Time and Temperature Effects on Glass in the Annealing Range. *By P. W. Collyer, Scientific Instrument Division, American Optical Company, Buffalo* 15, *N. Y.*

In the precision optical industry, the annealing of glass is extremely important because of three characteristics that are associated with such heat-treatment. These are freedom from stress, homogeneity of physical properties, such as refractive index and coefficient of expansion, and stability of these properties.

Fine annealing schedules are therefore required because, first, the slower cooling rates involved produce smaller temperature gradients throughout the work which in turn lead to greater freedom from stresses and greater physical homogeneity, and, second, the finer schedules yield a more stable condition of the glass. Since the time necessary to accomplish these various degrees of approach to the most stable state increases rapidly as the closer approach is made, the development of the most efficient schedules becomes more important economically in these cases.

The search for more efficient fine-annealing schedules led the author to obtain curves of refractive index versus time. The work was done on samples of borosilicate glass which had been rapidly quenched from a temperature of 1075°F by holding them for periods up to 500 hours at constant temperature. The refractive index for sodium light was measured for each sample (triple checked) by a Pulfrich Refractometer.

The equilibrium condition was attained to a very close approximation at several temperatures and this nearness of approach made possible the comparison of various proposed equations (Winter, Maxwell, McMaster and Tool) relating the change of properties to their equilibrium values.

After it was shown that equations expressing $\frac{dn}{dt}$ as first or second degree functions of (ne—n) did not seem to fit the present data, the equation proposed by Tool was transformed to give the following expression for the rate of change of index:

$$\frac{dn}{dt} = Q(ne - n)e^{\frac{n}{P}}$$

where

$$Q = M\,Ko\,e^{\frac{T}{g}}$$

t = time
n = refractive index
ne = equilibrium value of n
T = temperature
P, M, Ko, g = constants

It was shown that this equation appears to represent adequately the changes of index derived from the data obtained in this study and also those of previous investigators.

As a result of this study, an annealing schedule accomplishing an approach to the most stable condition was worked out which decreased the time from 12 days to about 7 days.

Attack of Glasses by Alkaline Solutions. *By R. D. Smith and P. E. Corbin, Corning Glass Works, Corning, N. Y.*

The glasses used in this investigation consisted of a borosilicate glass, a soda-lime glass and a lead glass, all of which were normal compositions. Each solubility determination was made in duplicate, two samples of the glass being placed in each container. The samples were in the form of glass tubing of 20 to 25 cm^2 area and the containers were Pyrex brand test tubes. The glass samples were washed in distilled water, dried at 110° C., cooled in air and weighted. This treatment was repeated after the solubility run and the loss in weight computed in milligrams per sq. cm. of glass exposed for 18 hours treatment at 90° C. in the respective reagent. The reagents used included sodium hydroxide, sodium carbonate, sodium silicate and potassium silicate of various normalities and silica to alkali ratios.

The attack of glasses by NaOH, Na_2CO_3 and a number of other alkaline solutions followed a reasonably well expected course in the solution of the glasses according to the normality and pH of the solutions. The sodium silicates in concentration under 0.5 Normal Na_2O also showed a similar attack trend. With Na_2O Normalities above 0.5N some sodium silicate solutions show greater glass attack than do corresponding NaOH solutions of equivalent Na_2O normality. Since it has been generally accepted that NaOH in equivalent normalities had the greatest effect on glass attack of the alkaline solutions, it is rather interesting to note that these certain sodium silicate solutions of equivalent alkaline normality (above 0.5 N) and of decidedly lower pH values are actually the more corrosive toward glasses.

It was also shown that the SiO_2 to Na_2O ratio for maximum glass attack depends upon the glass composition and is different for a borosilicate, a soda-lime or a lead glass. Potassium silicate has a behavior similar to sodium silicate in the attack on the three glasses.

As the knowledge of the mechanism of chemical attack on a glass surface is not very complete, it is hoped that the effect of silica as an accelerator in the alkaline attack of glass may provide some further knowledge toward the mechanism of glass attack by alkaline solutions.

These findings do not discredit the use of alkaline silicates in detergents and cleaning compounds for glass cleaning purposes since the Na_2O normalities in such solutions are well under 0.5 N.

Possible Colors of the Future. *Presented before the Design Division by W. A. Weyl, Glass Science, Incorporated, State College, Pa.*

While the number of colorants available to the ceramist is extremely limited and their possibilities well investigated, this does not mean that research on ceramic colors has come to an end. Such research has taken two lines, the first being the study of the how and why. This has for its purpose the better understanding and controlling of colored glasses.

For example, studies on the striking of gold ruby glass revealed the role which tin compounds play in the batch formula. It was discovered that the presence of tin compound increases the solvent power for metallic gold or copper and, as a result, it imparts a property characteristic of heavy lead crystal glasses to a soda-lime glass. Likewise, a study of the functions of various constituents in a selenium ruby batch has lead to a better understanding of the nature of such a glass. Research on electrolytic methods of controlling the state of oxidation while it does not aim directly at new colors opens up the possibility of making certain colors safer to reproduce.

The other line of research is dealing with studies of colors produced in unusual glass compositions. For example, the development of alkali-free fiber glass, silica-free phosphate glasses and rare-earth borates are offering interesting fields for color studies.

(*Continued on page* 316)

GLASS COLORS BY PEMCO AND SERVICE TOO!

Thirty six years of porcelain enamel leadership imposed a responsibility that PEMCO gladly accepted in the development of this Glass Color Division. It is a responsibility that never recognizes "the just as good" attitude. It must be better or it isn't PEMCO. As an example—PEMCO Bottle colors. It is one of PEMCO requirements that these colors stand up under strong caustic and mild acid solutions—that they match the coefficient of thermal expansion of the container so that even under pressure of carbonation there will be no breakage due to color application. The Pemco Colors you receive for beverage containers are warranted to perform in a most satisfactory manner— and there, too, is a service that matches the quality of the products. Ask about it.

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Sodium Sulphate
Sodium Carbonate

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IMMEDIATE SALE

• In natural surface lake deposits located in Wyoming, just off Highway 287, midway between Casper and Rawlins; has never been accurately surveyed; high spot estimates indicate at least 500,000 tons of sulphate and 28,000 tons of carbonate waiting for development; any reasonable offer, preferably on royalty basis, will be considered; inquiries for further detail invited.

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ALKALI COMPANY
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THE GLASS DIVISION AT ATLANTIC CITY . . .

(*Continued from page* 314)

There also exist possibilities in new fields such as that opened up by new light sources, especially those producing ultra-violet radiation. By such light, it is possible to excite certain glasses and pigments to brilliant fluorescence. Through the use of such a combination, color effects are produced which cannot be obtained in ordinary light and it may be possible that they can be used in the field of advertising and in unusual displays.

LACLEDE-CHRISTY ANNOUNCES APPOINTMENTS

Appointment of Paul J. Maddox as General Sales Manager of the Refractories Division and John B. Ives as Manager of Operations has been announced by Laclede-Christy Clay Products Company.

Mr. Maddox joined the company in 1932 starting as a direct salesman. Since then, he has acted in various capacities for the Sales Department, principally heading dealer and agent sales, high temperature specialties and the Arch and Wall Division.

Mr. Ives, who will have complete charge of the manufacturing and mining operations of the company's St. Louis and Toledo plants and mines, brings to his new position over twenty years of varied experience in all phases of the company's manufacturing operations. For many years he was Superintendent of the Toledo plant and for the past five years, has been General Superintendent of Plants and Mines.

PITTSBURGH PLATE REVAMPS HOUSE MAGAZINE

Pittsburgh Plate Glass Company has issued the first number of its completely changed house magazine, *Pittsburgh People*. The publication is scientifically planned and is the result of several months of intensive research and effort. Under the new plan, several steps were taken which had not been used before, such as new and unusual uses of tools and media employed in industrial research, production, distribution, advertising and marketing, special personnel selection and training, as well as innovations in mechanics of reporting and editing.

Heading the staff of the new *Pittsburgh People* is Norman L. Park, Manager of Publication for the company. Charles A. Betts is Associate Editor.

PENNSYLVANIA SALT PLANT IMPROVEMENTS

The Pennsylvania Salt Manufacturing Company has announced that it now has under construction at its Wyandotte plant additional boilers and allied power generating equipment, including a completely new modern power plant building, at a cost of more than $3,500,000.

In addition to new equipment, Pennsalt is installing fly ash collectors for the present three large pulverized-coal burning boilers. The collectors will remove solid products of combustion in the flue gases in an amount equal to or better than existing municipal requirements.

In the existing boilers, the company is installing new induced draft fans and new motors to take care of the additional draft loss placed on the boilers by the fly ash collecting equipment in the duct system through which products of combustion are discharged.

SHIFTING SANDS *of* DEATH VALLEY

The Hollywood motion picture people frequently use the Death Valley Sand Dunes as a natural backdrop to establish a desert "locale." You've seen these sand dunes in numerous motion pictures, creating the illusion that it might be at some distant place, such as the Sahara Desert.

Seas of sand, made up of countless millions of grains parched with the desert heat, constantly shifting in the wind and creating new studies of light and shadow in the quiet atmosphere of Death Valley.

It was here in the heart of Death Valley, California, where the original discovery of Borax was made, necessitating the development of the famous 20 Mule Team caravans, to haul the much needed borax ore to the outside world.

MELTING—The workability and quality are quite dependent upon the melting operation. A batch easy to melt and of satisfactory viscosity will produce a homogeneous glass and one which can be readily worked and formed. The fluxing action of Borax will assist in securing these optimum conditions.

Another good reason why Borax should be used as an essential ingredient in the batch formula.

Our representatives are prepared to discuss the special advantages of B_2O_3 in glass.

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New 40 cu. ft. Smith Glass Batch Mixer equipped with dust boot which confines dust within mixer drum.

Smith Glass Batch Mixer in discharge position. Fast "Tilt and Pour" discharge.

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The Smith duo-cone drum is famous for its effective "end-to-center" mixing action. Vertical cascading and unnecessary agitation are avoided by substituting a less violent rolling action. Segregation is eliminated, for mixing continues during the entire discharge cycle. Discharge is fast and complete. No corners or pockets in drum. No "left overs" to contaminate succeeding batches. Insures improved quality of glass batches and greater production. Built in all standard sizes up to 112 cu. ft. Write for bulletin.

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SMITH
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Glass Batch MIXERS

(*Continued from page* 307)

the procedure. The average deviation from 100 per cent for these twelve samples is about 4 per cent.

From the standpoint of the glass industry, this procedure seems to have some merit for the rapid estimation of the chemical composition of glasses. While spectrochemistry has been used for minor ingredients or tracer elements in glass technology problems, little success has been made in using it as a tool to replace the old chemical methods for glass analyses. Techniques such as these may pave the way for more rapid reporting of results.

The Color of Heavy Lead Silicate Glass

In investigating the coloring effect of iron oxide, chromium oxide and copper oxide in heavy lead silicate glasses, W. M. Hampton *(Nature,* 158, [4017], 582, 1946) found that to a glass with a refractive index of 1.915, iron oxide gave a yellow color, copper oxide a green, and chromium oxide a yellow, when viewed through a 2 cm. thickness at concentrations of 0.01, 0.005 and 0.0005 per cent, respectively. Spectrophotometric measurements indicated that the coloring effect of each oxide was proportional to its concentration over the range studied. The comparative coloring power for iron oxide, copper oxide and chromium oxide was in the ratio 1:2:40, respectively.

To produce a glass as free from color as possible, pure lead nitrate was prepared by dissolving spectrum pure lead in nitric acid and precipitated silica was obtained by distillation from sodium silicofluoride and sulphuric acid. Sintering and melting the batch in a thoria crucible produced a glass free from any noticeable tint through a 5 cm. thickness, the refractive index of the glass being 1.90.

CORNING TO ERECT NEW BUILDINGS AT CHARLEROI PLANT

Contract for the design and construction of two new buildings at the Charleroi, Pa., plant of Corning Glass Works has been awarded to The Rust Engineering Company, according to a recent announcement. Approval of the project, which is expected to be completed by October 1, was granted by the Civilian Production Administration.

The new buildings, a finishing building 25,000 square feet in area and a furnace building approximately 10,000 square feet, will in effect be additions to present structures in the company's Middle Factory. They will provide additional melting capacity and general floor space to accommodate enlargement of Corning's television bulb program. The bulbs will be made by both hand and automatic production methods and will range in size from a face diameter of 7 inches to 15 inches. A new annealing oven will also be installed to take care of the increased capacity.

In addition to the new buildings, which will be of brick and steel construction with corrugated siding, a radial brick chimney 135 feet high and having an interior diameter of four feet will be constructed to serve the furnace building.

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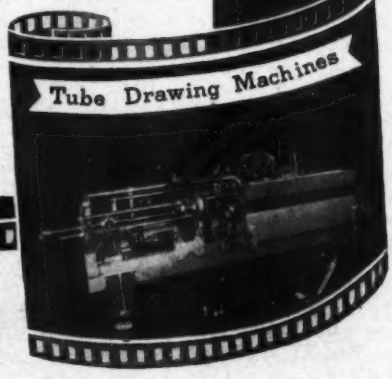
Appraisals



AMSLER MORTON CORPORATION
CHAMBER OF COMMERCE BLDG., PITTSBURGH 19, PA.

G.C.M.I. HOLDS ANNUAL MEETING . . .

(*Continued from page* 290)

inception of the Institute, it has really been standing by marking time awaiting the removal of restrictive wartime governmental controls which dictated types of containers which could be made, for whom they could be made, how many containers could be made and for what they could be sold. With the removal of these regulations, the Committee on Market Research and Promotion has become activated and Mr. Schrag presented his Committee's recommendations for an aggressive and concerted program of market study and promotion which, if finally adopted and implemented by the appropriation of adequate funds, should go far in adding new vigor to the sales curve of the glass container industry.

A resolution was passed approving a proposal for the necessary funds and referred to the Board of Trustees. The program will become a reality when a majority of the membership finally approves the assessment to provide the promotional budget.

Dr. Kenneth C. Lyon, Chairman of the Committee on Testing Procedures, started the second day of the meeting with a report on the varied work of his Committee.

Among other things, in referring to Bulletins and Publications, Dr. Lyon stated that Bulletin No. 9, "Glass Plant Guide to Identification of Stones in Glass" by Dr. M. A. Knight of Preston Laboratories, has been issued in the form of a reprint from the February, 1947, issue of THE GLASS INDUSTRY.

In broadly outlining research activities of his Committee, Dr. Lyon stated that it was felt advisable to continue research along lines pertinent to the study of the strength of glass. He stated that there have been several valuable and practical sidelines developed from these and related studies. The schools conducted by the staff of Preston Laboratories on breakage diagnosis, Dr. Lyon stated, "has assisted in the rational solution of some otherwise baffling problems encountered in every day operations."

Dr. Lyons outlined the work which has been done on cord research mentioning the employment of the density comparator for routine evaluation of glass densities and the centrifuge-density technique.

These two methods dealing with cord investigation, it was stated, seem to cover immediate needs. However, Dr. Knight has been asked to prepare a rather detailed summary of the work on this problem.

Another study which Dr. Lyon briefly touched upon was that of the apparatus used in connection with impact research. This apparatus measures the speed at which glass cracks under impact from a mechanical hammer. The apparatus including an electronic circuit connected to a cathode ray oscillograph records the time for the crack to pass between two points about two inches apart. The fracture of glass is slightly less than a mile a second according to the results indicated on the oscillograph.

Dr. Lyon explained that the immediate aim of the present phase of investigation is to determine if the speed of fracture is influenced by atmospheric conditions (chiefly moisture) and temperature as it seems the strength of glass is affected.

In closing his report, Dr. Lyon mentioned the Ware Tester Schools being conducted.

The report of the Committee on Government-Industry Relations was presented by Mr. Lewis F. Gayner in view of the resignation of Mr. C. D. King who served as Chairman of the Committee until April 8, 1947.

Mr. Gayner's report briefly summarized the Committee's activities by outlining its contacts and cooperation with the former Civilian Production Administration, now the Office of Temporary Controls. He pointed out that at the time of the presentation of his report, ten orders remained in effect of which only four directly or indirectly concerned the glass container and closure industries. The four orders are M-43, which restricts the use of tinplate for closures and the use of foil for liners and also provides for allocation of pig tin for various permitted uses resulting in the control of the available quantity of tinplate.

Indirectly affecting the glass container and closure manufacturers are orders M-81, M-21 and R-1. Order M-81 restricts the weight of tinplate that may be used in the manufacture of tin cans. All quota restrictions were removed on December 27, 1946, and on March 7, 1947, M-81 was further amended to remove specifications and limits on the size of cans permitted to be manufactured. Order M-21 concerns the export of tinplate, and order R-1 regulates the sale and distribution of natural and synthetic rubber with the exception of neoprene.

Following Mr. Gayner's report for the Government-Industry Relations Committee, Mr. Fred E. Fuller, General Counsel of the Institute, spoke briefly on the new Trade-Mark Law, referred to as the Lanham Act, which becomes effective July 1, 1947. Trade mark law and this particular legislation seem to be a very involved subject. However, Mr. Fuller succinctly outlined some of the features of the new law as it relates to the glass container industry and he strongly urged that all members of the Institute acquaint themselves with the details and ramifications of the new law in order to obtain full advantages of its provisions.

The next report was given by Mr. S. B. DeMerrell who heads the Committee on Container Design and Specifications. Mr. G. A. Mengle, Chairman of the Sub-Committee on Beer Bottles, and Mr. R. M. Lamb, Jr., heading the Sub-Committee on Milk Bottles, also presented their reports.

Mr. DeMerrell stated that since the last report of the parent committee was presented to the industry, much progress has been made in revising and adopting container standards. He outlined the fact that a number of the former G.C.A. Drawings of Containers which were not in general usage by packers have been discontinued. Mr. DeMerrell also stated that during the past two years, twenty-one of the former drawings have been re-engineered and issued on G.C.M.I. Drawing forms and are now in use by the industry. It was pointed out that the Technical Sub-Committee is now engaged in checking and re-engineering the specifications for a considerable number of former G.C.A. Drawings in preparation for the issuance of G.C.M.I. Drawings to cover these lines.

Mr. Mengle discussed the progress made with the 1-Way beer bottle and, through the courtesy of Owens-Illinois, showed a colored moving picture of the single

(*Continued on page* 322)

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RESOURCES. With your plant for the manufacture of glassware and glass containers located conveniently at New Orleans, you'll have low cost natural gas readily available in vast quantity from the great fields nearby. Two ancient sea terraces just 50 miles away provide unlimited sources of glass sand. Soda ash, limestone and other needed materials are also close at hand.

MARKETS. From your strategic New Orleans plant location—foreign, national, regional and local markets may be served most efficiently, most economically: 150,000,000 buy-minded Central and South Americans—52,000,000 residents of our rich, 22-state Mid-Continent area—the 10 Southern states with 23% of the nation's population—and a growing New Orleans market with numerous manufacturers of food products; bottlers and breweries. *There is no glass manufacturing plant within approximately 200 miles of New Orleans.*

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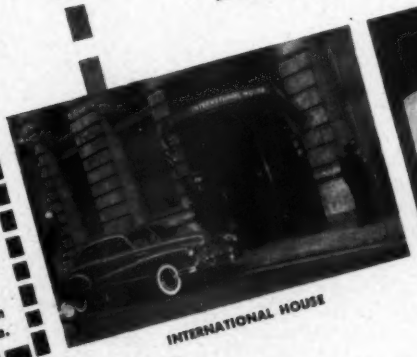
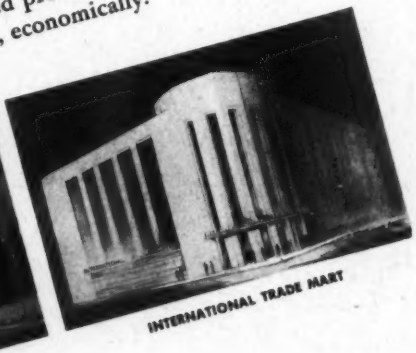


INTERNATIONAL HOUSE



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G.C.M.I. HOLDS ANNUAL MEETING . . .

(*Continued from page* 320)

trip bottle operations as carried on by the Acme Brewing Company of California.

Mr. Lamb, in reporting on the activities of the Sub-Committee on Milk Bottles, stated that since his last report the energies of his group have been directed at bringing to completion two principal programs which were begun more than a year ago. He stated that the Manual of Standards for the Dairy Industry has been completed. The other project, Mr. Lamb said, whose objective is uniformity of weights and measures regulation on milk bottles, is well on its way to success.

Mr. Harry W. Kuni, Secretary-Treasurer of the Institute, in the absence from the meeting of Mr. G. M. Stuntz, Chairman of the Committee on Standards and Finishes, presented this Committee's report.

Mr. Stuntz's report enumerated the objectives of his Committee as "1) determining whether the present specifications are the most satisfactory from the viewpoint of all concerned, the mold maker, glass container and closure manufacturers, packers and the ultimate user of the packaged product, 2) the discontinuance of sizes that are no longer in demand or in active use, 3) the simplification and clarification of the data contained on the prints to remove superfluities or ambiguities and make them more readable by shop personnel."

Further on in his report, Mr. Stuntz detailed the extent to which these objectives have been attained.

As is customary with Institute meetings, a golf tournament was arranged and a bridge party was arranged for the ladies. Attractive prizes were donated by members for both affairs and it should be mentioned that the winner of the golf tournament, Mr. Fred Dundas of Dominion Glass Company, in addition to carrying off the first prize, also was presented with a plaque donated by the Gayner Glass Works.

At the close of the meeting, it was announced that the fall Semi-Annual Meeting has been scheduled to be held at the Sea Isle Hotel in Miami Beach early in November.

Lee W. Minton, President of the Glass Bottle Blowers Association of the United States and Canada, as a member of the United States Labor Delegation visited Argentina a few months ago for the purpose of studying Argentine workers' organizations. A brief report of Mr. Minton's visit appeared in the May issue of THE GLASS INDUSTRY. Unfortunately a photograph purporting to be that of Mr. Minton was erroneously used with this story. We're sorry. The real Mr. Minton is to the right.

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Fiberglas is a truly basic material — an engineering material just as steel and aluminum are and, like them, it is produced in a great variety of types and forms.

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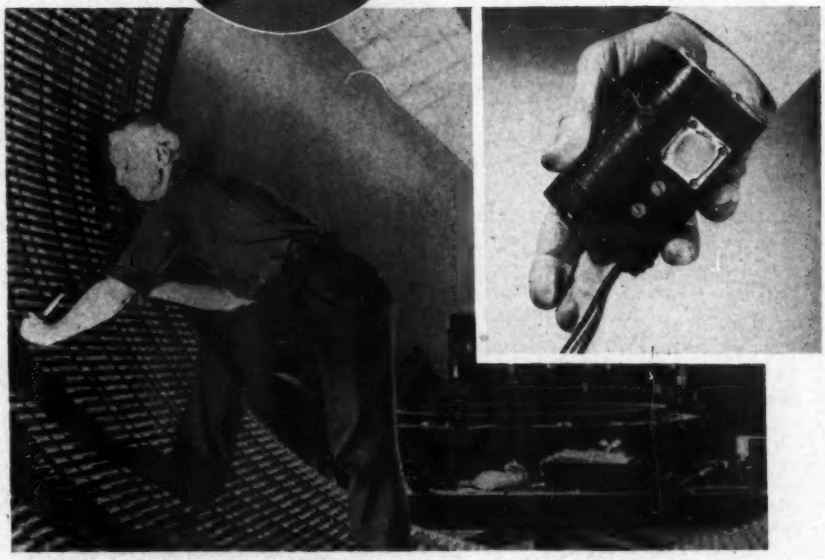

Midget or Monster Motors. Fiberglas in textile form provides an unsurpassed base for electrical insulating impregnants. Fine filaments of glass, specially formulated for electrical uses, are twisted into yarns to be served on wires This 15-ton stator for a ship's motor used 70,000 miles of Fiberglas yarn in its coil insulation.

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(*Continued from page* 302)

low temperature volume conductivity of glass is one of the most convincing in this respect. Besides, a glass surface brought in contact with the compounds of monovalent ions, such as Li^+, Ag^+, Tl^+, enters a chemical reaction which does not affect the silicate network but can be described as a "base exchange" reaction. Reactions of this type are common with certain silicate minerals having an open structure. One often refers to these reactions as "zeolitic" because a group of minerals, the zeolites, have a high base exchange capacity. Base exchange reactions usually lead to an equilibrium, but by combining one reaction, such as

$$Na^+ \cdot \text{glass} + Ag^+ = Ag^+ \cdot \text{glass} + Na^+,$$

with another leading to the absorption of the Na^+, such as

$$Na^+ + \text{clay} = \text{sodium aluminosilicate} + \text{water},$$

the equilibrium may be shifted far to the side of the Ag^+ glass. This process is used commercially for producing silver stain.

Recently, we discussed these reactions in detail in connection with their application to the staining of glass by means of copper and silver.[27] A base exchange reaction involving the substitution of Li^+ for Na^+ has been suggested as a qualitative test for Li^+. This substitution leads to porosity and to corrosion of the glass surface.

As mentioned in a previous paper,[6] base exchange reactions of the hot glass with metal chloride vapors can be used to examine the alkali distribution within a surface layer. In the temperature range below the strain point, the base exchange consists, more or less, of replacement of alkali ions by other monovalent ions.

With increasing temperature the base exchange is no longer limited by the valency of the exchanging ions. Accompanied by an ionic rearrangement, even tetravalent ions such as Ti^{4+} and Sn^{4+} can replace alkali. Reactions of this type involving Bi^{3+}, Fe^{3+}, Sn^{4+} and Ti^{4+} have been widely used in the past for producing iridescent glasses or luster colors. The iridescence is caused by interference of the light reflected from the surface of the film having a high refractive index and that reflected from the glass-film interface. Surface films containing Sn^{4+}, Bi^{3+} or Ti^{4+} have a higher refractive index than the bulk of the glass.

Reactions of this type remove alkali from the surface in the form of sodium chloride. They can be used, therefore, to improve the chemical resistivity of glassware. In addition, there are sound reasons for expecting that a treatment of glass with metal chloride vapors will lead to a noticeable improvement of its mechanical properties.

The strength of glass fibers and the lifetime of glassware depend on the vulnerability of the surface. As pointed out previously, the "hardness" of a glass surface in this respect is not identical with the hardness used for describing minerals. The mutual scratching of two glasses consists of a seizure due to chemical bonds and of their subsequent breakage. The "scratch hardness" or surface vulnerability should be improved, therefore, if the chemical reactivity of the glass surface is decreased by withdrawing alkali from the surface layer.

In addition to this chemical effect which aims at the improvement of the surface vulnerability, a treatment with metal chloride vapors should directly improve the impact strength of glassware by bringing its surface layer into a state of compression. The mechanism of this reaction has been described in detail in a paper on "The Strength of Glass as Affected by Dealkalizing Its Surface."[28]

Since it is not possible to evaluate the improvement of the mechanical properties of glassware by this exposure to metal halide vapors in laboratory experiments, actual plant tests would be highly desirable.

4). *Dealkalization of the glass surface.* The influence which the removal of the alkali ions from the glass surface exerts upon the various properties was the subject of a recent paper by H. S. Williams and W. A. Weyl.[6] In this and subsequent papers,[28,1] the writer pointed out that dealkalization not only improves the chemical resistivity and electric insulation but also has a decisive influence upon such mechanical properties as impact strength and scratch hardness.

The first observations concerning the relation between chemical resistivity of a glass and removal of alkali from the surface go back to G. Keppeler[29] and his students. Their studies centered around the influence which annealing has on the chemical resistivity of glass. A distinction had to be made between the bulk of the glass and its surface. The discovery that combustion gases can improve the chemical resistivity of a glass surface several hundred per cent led to the development of methods which produce the same effect in electrically heated lehrs. Keppeler's findings were confirmed by a A. Cousen[30] and C. J. Peddle.[31] A systematic study of the interaction between the surface of a soda-lime glass and an atmosphere containing sulfur dioxide was carried out by J. N. Coward and W. E. S. Turner.[32]

Reactions between soda-lime glasses and combustion gases lead to the removal of Na_2O from the surface, according to the equation:

$$Na_2O + SO_2 + 1/2O_2 = Na_2SO_4$$

They require relatively high temperatures because they involve the migration of oxygen ions which are strongly bound in the glass structure: reactions involving the breakage of Si-O bonds have a high activation energy.

In the low temperature range, alkali can be removed from a glass surface by a base exchange reaction similar to those described in the previous chapter. Base exchange reactions between the sodium ions and other monovalent ions do not require the breakage of Si-O bonds; their activation energy, therefore, is low so that they can proceed with reasonable speed even at room temperature. Reactions of this type do not remove Na_2O as a unit but replace Na^+ by H^+, Ag^+ or Cu^+. One possible method of removing Na_2O from the glass surface consists of replacing the Na^+ by H^+ by means of a low temperature base exchange reaction and driving out water at higher temperatures. Leaching out a glass surface with diluted acids at room temperature leads to a hydrogen glass. Subsequent baking at 500°C causes the hydrogen ions to escape in the form of water.

The above mentioned paper by H. S. Williams and W. A. Weyl[6] describes a new method of dealkalizing the glass surface by means of clay. The mechanism of this reaction is also a base exchange between the sodium ions and hydrogen ions of the clay:

$$Na^+ \cdot \text{glass} + H^+ \cdot \text{clay} = H^+ \cdot \text{glass} + Na^+ \cdot \text{clay}$$

The superiority of clay and similar substances as donors of hydrogen ions over the leaching with aqueous solu-

tions of acids is due to their making available H^+ ions at high temperature (up to 400°C) where the base exchange is fast and consequently has considerable depth action. Above 400° to 500°C, the resulting hydrogen glass is unstable and decomposes under liberation of water. As a result of the two reactions, Na_2O is removed from the glass surface.

Dealkalization of the glass surface by means of clay treatment is very efficient, but the amount of handling of the ware prohibits its practical use for most purposes. A recent study of this process by F. R. Matson[33] gives a picture of the effect of this treatment on glass containers under plant conditions.

The method for improving the chemical durability of glass described by H. S. Williams and W. A. Weyl was tried in the Research Laboratory of the Armstrong Cork Co.

"Two groups of 8-ounce flint whiskey flasks of similar composition were used for the test. Each group was divided into three sets for different surface treatments as follows: a) Normal run of untreated bottles. b) The flasks were coated on the interior with a slip of levigated kaolin and then fired to 400°C for three hours in an electric furnace. The clay was then washed from the glass surfaces with distilled water. It was difficult to scrub the clay entirely out of the bottles because the shoulder areas were not readily reached with a brush, and the clay adhered well to the glass. It never was removed from a few hairlines in the surface. After the washing was completed, the flasks were rinsed three times with doubly distilled water. c) Untreated bottles were scrubbed on the interior with a brush and distilled water to simulate clay removal. They were then rinsed three times with doubly distilled water. This group was included in the test because water rinsing may remove some alkali from the glass surface.

Both groups of bottles were then tested for chemical durability by filling them with doubly distilled water and placing them, covered with small Pyrex brand beakers, in an autoclave which was then raised to 121°C (15 lbs. steam pressure) on a carefully controlled schedule in thirty minutes, held at that temperature for one hour, and reduced to 100°C (0 lbs. steam pressure) in thirty minutes, again on a controlled schedule. A 100-ml. portion of water from each flask was titrated against 0.02N H_2SO_4 and the results were recorded in terms of milligrams of NaOH per liter extracted from the glass. Further details of the method can be found in 'Variable Factors in Accelerated Autoclave Chemical Durability Tests' by J. S. Owens and E. C. Emanuel.[34]

The results of these tests are given in Table IV.

TABLE IV

	mg. NaOH/l Extracted Av.	No. Tested	mg. NaOH/l Extracted Av.	No. Tested
Normal run	13.5	12	13.3	12
Water scrubbed...	12.5	6	11.6	6
Clay treated	2.2	6	2.4	6

Water washing had only a slight effect. The clay treatment at 400°C greatly improved the chemical durability

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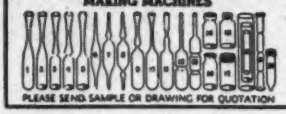

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of the bottles, as was predicted by Williams and Weyl in their tests of microscope slides."

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ARTHUR D. LITTLE ELECTS VICE PRESIDENT

Leroy F. Marek has been elected Vice President of Arthur D. Little, Inc., according to an announcement following a meeting of the Board of Directors.

Mr. Marek joined the company in 1934 and has been in charge of its chemical engineering activities for several years. He is a graduate of the University of Texas and received his master's degree from Massachusetts Institute of Technology, where he served as Acting Director of the Research Laboratory of Applied Chemistry before joining Arthur D. Little, Inc.

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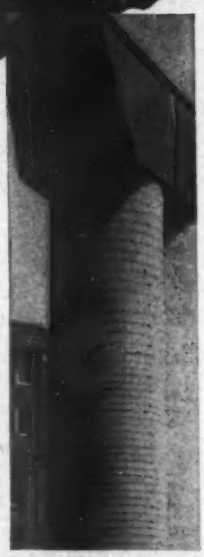

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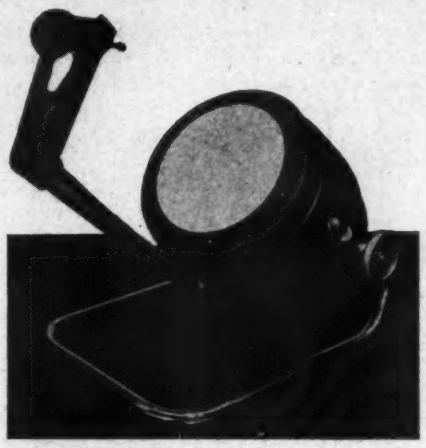
DIAMOND ALKALI ELECTS PRESIDENT

Raymond F. Evans has been elected President of Diamond Alkali Company to succeed John T. Richards who has announced his retirement as President and Chairman of the Board. The announcement was made following a meeting of the Board of Directors at the annual stockholders' meeting.

Raymond F. Evans

Mr. Evans joined the company in 1931 after leaving Princeton University where he majored in chemistry. After five years of operational experience, he was placed in charge of a small experimental unit and laid the framework for the large research and development unit the company now has. He has served as head of the Research Division, President of Diamond Magnesium Company (a United States-owned war plant operated by Diamond Alkali Company) and as Vice President and General Manager of the company's Painesville plant.

Mr. Richards joined Diamond Alkali Company in 1917 as a clerk and gradually rose through the ranks to become President in 1937 and Chairman of the Board in 1943. Prior to becoming President, Mr. Richards was Assistant Secretary, Vice President and Executive Vice President. He will continue as a Director.



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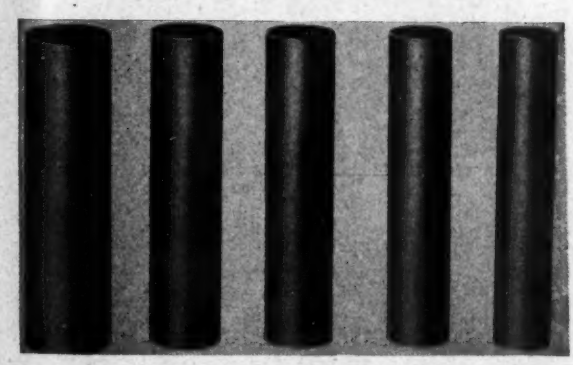

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